# ~~AN~~ INVESTIGATION OF ~~THE~~ SIMULTANEOUS TRANSFER OF TWO SOLUTES IN A LIQUID-LIQUID ~~SYSTEM~~ EXTRACTION

A thesis submitted
for the
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by

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## ABSTRACT

The separate and simultaneous transfer of phenol and propionic acid between two laminar co-current streams of carbon tetrachloride and water was investigated. Equilibrium interfacial tensions and equilibrium distribution data were determined and the latter correlated by a simple empirical equation for each solute over the concentration range 0.01 to 0.3 Molar in the carbon tetrachloride phase. Two new designs of experimental apparatus were developed: a wetted wall column (contact time 0.5 to 10 seconds) and a horizontal contactor (100 to 900 seconds) with provision for schlieren photography.

Both solutes were found to produce spontaneous interfacial disturbances ("eruptions") during mass transfer in either direction. An expression was derived for the variation of interfacial tension with time in a freshly contacted liquid-liquid interface. These results were used to correlate the relative strengths of the eruptions at different solute concentrations.

The Danckwerts theory of mass transfer across an interface by penetration with surface renewal was adapted to the case of a freshly contacted liquid-liquid interface. The resulting equations express the mass transfer as a product of three factors: the "penetration" coefficient of mass transfer, the mean

concentration driving force, and a function of the product of contact time and surface renewal rate. Experimental results agree with the hypothesis that mass transfer in the eruptive regime can be described in terms of penetration and surface renewal.

Low results for transfer of propionic acid from water to carbon tetrachloride were interpreted in terms of an interfacial resistance caused by hydrogen bonding between the aqueous phase and the acid molecules.

# INTRODUCTION

Many processes of interest to chemical engineers involve the diffusion of material across a phase boundary. Since an interface forms the zone of transition between the intermolecular forces of two phases, the question arises as to whether mass transfer across this zone is subject to any special influences.

One possible effect would be resistance to mass transfer across the interface. Experimental work on this subject, both for liquid-liquid and for gas-liquid interfaces, has been inconclusive or contradictory, because of difficulties in determining the interfacial conditions of temperature, concentration and flow pattern, (§§ 1.1 to 1.6), [46]. The presence of such interfacial barriers might be expected to affect differentially the simultaneous transfer of two different (e.g. polar and non-polar) solutes.

Another effect, which has been the subject of some attention in recent years, is the occurrence of spontaneous interfacial disturbances ("eruptions") during mass transfer, [1], [30]. It is now generally accepted that they are due to the formation of local gradients of interfacial tension caused by local variations of solute concentration in the interface. It can be argued that such "eruptions" would cause considerable portions of the

interface to be replaced by fresh liquid from the interior, and thus result in an increase of the rate of surface renewal; this may mean that for solutes of different interfacial properties the rates of mass transfer may be different even under conditions of equal flow parameters of the bulk phases and equal diffusivities. No conclusions can thus be drawn from such experiments about the effects of molecular diffusivity on the transfer process. If, however, the transfer of the two solutes takes place simultaneously - i.e. under the same interfacial flow conditions - some conclusions can be arrived at.

In order to test these possibilities, experiments were conducted on the separate and simultaneous transfer of propionic acid and phenol between carbon tetrachloride and water. It was necessary to determine distribution coefficient and interfacial tension data for this system (chapter 3). Also, since the hydrodynamics of existing forms of liquid-liquid contactor were uncertain, two contactors were developed in order to obtain a rational basis of comparison for the mass transfer coefficients: namely, vertical and horizontal laminar co-current liquid-liquid contactors with moving interface (chapter 2).

The limits of applicability of the various mass transfer theories to liquid-liquid extraction are still

unknown, largely because of the many complicated ways in which the liquid interface can be affected, such as deformation, oscillation, differential motion under interfacial tension, and surface renewal. Each of these can change the flow pattern of the associated fluid substrate. The relevant theories are reviewed in chapter 4. In particular the penetration equation as presented by Bhattacharya and the surface renewal theory of Danckwerts are selected as most likely to apply to the experimental results; the latter is modified to take into account the small contact time of a wetted wall column, and combined with the former to fit the case of liquid-liquid diffusion ( § 4.3).

Results and conclusions are presented in chapter 5, with a review in § 5.9.

# CHAPTER ONE

## Literature Survey of Interfacial Effects in Liquid-Liquid Mass Transfer

1.1 WARD and BROOKS [1] from considerations of interfacial tension and adsorption, suggested the possibility of a free energy of adsorption barrier, somewhere between 1 and 10 Kcal per mole, for mass transfer in either direction across a liquid-liquid interface. They performed experiments on the diffusion of acetic, propionic, n-butyric and n-valeric acids across an unstirred stationary water-toluene interface, using an optical method - the Lamm scale - to follow the course of diffusion. Theoretical equations were derived on the basis of no interfacial resistance, and were found to agree with experimental results for acetic and propionic acids. Hence the authors concluded that the interfacial free energy barrier must be less than 4 to 7 Kcal per mole (corresponding to an interfacial resistance coefficient $K_i$, such that $10 < K_i^{-1} < 10^3$ sec. $cm^{-1}$); the limits being set by the accuracy of the Lamm scale method, which was capable of measuring interfacial concentration gradients only for contact times $>$ 10 minutes (by which time the ordinary overall bulk diffusional resistance coefficient would be $K_R^{-1} > 10^4$ sec $cm^{-1}$). The valeric and butyric

acids were found to give rise to spontaneous interfacial agitation, which caused intense but very localized stirring within one millimetre of the interface.

1.2 TUNG and DRICKAMER [4] reported an interfacial resistance to the transfer of sulphur dioxide in the system $SO_2$ - n-heptane, and of sulphuric acid between phenol and water. Using $S^{35}$ as a radioactive tracer, they plotted counts per minute versus time in an unstirred cell packed with fine mesh, and compared the results with their solution of the diffusion equation for the cell. Discrepancies between theory and experimental results were attributed to initial convection currents. Unusually high interfacial resistances were found - approximately $10^5$ cm. per sec.

1.3 LEWIS [2] performed experiments on a variety of liquid-liquid systems in a new type of stirred cell. In some cases he found lower than normal mass transfer coefficients - as defined by his empirical correlation - notably with transfer of organic acid and base between water and an aprotic solvent such as carbon tetrachloride. The lower coefficients were attributed to a slow interfacial reaction of solute hydration or dimerization. Resistance coefficients were from 500 to 7000 sec $cm^{-1}$. Higher than normal mass transfer coefficients were also

found, associated with the observation of spontaneous interfacial turbulence. Addition of surface active agents, which formed rigid interfacial films, such as collodion or protein, caused a decreased rate of mass transfer in all cases. LEWIS attributed this decrease to the increased surface viscosity, which lowered the eddy diffusivity near the interface. Surface active agents which formed mobile monolayers were not found to decrease mass transfer significantly, except in one instance. Hence it was suggested that such monolayers may be very specific in their action.

1.4 Similar experiments were performed by BLOKKER [5] who obtained similar values for mass transfer coefficient - $K \approx 10^{-3}$ cm $sec^{-1}$ - and for interfacial resistance - $500 < K_i^{-1} < 5{,}000$ sec $cm^{-1}$. (The author notes that, since deviations from the correlation of LEWIS, on which all calculations of normal transfer coefficients are based, may amount to $\pm$ 50%, the smaller resistances are somewhat uncertain). In particular, he found resistances of 500 and 1000 sec $cm^{-1}$ for the system toluene-water-propionic acid (cf. WARD and BROOKS, § 1.1). Influence of several surface active agents was found to vary, being negligible in two systems and producing a decreased mass transfer coefficient in the third. (All three systems seem to have abnormal coefficients even before addition of surface

active agents - the first two are 75% lower than the correlation, the third is 200% higher.)

1.5 An explanation for the decreased mass transfer coefficient on addition of surface active agent was put forward by MAYERS [3], who worked with the LEWIS stirred cell, for which he produced an improved correlation. Using an improved surface viscometer, MAYERS showed that surface viscosity was of less importance than surface compressibility in causing a lowering of mass transfer rate. Thus he did not differentiate primarily between "rigid" and "mobile" interfacial films, (cf. LEWIS, § 1.3) but, using a variety of surface active agents, was able to detect in all cases a decrease in the coefficient, though sometimes small enough (20%) to have been overlooked by previous workers. From observation of the contraction and expansion of rafts of talc particles on the interface, he concluded that stirring caused some areas of the interface to be cleared by liquid arriving from the bulk of the solutions, thus leading to increased mass transfer through surface renewal, and that these lateral surface clearing movements were opposed by the surface pressure of the surface active agent. Both theoretically and experimentally he demonstrated the existence of a concentration of surface active agent at which lowering

of the mass transfer rate was at a maximum. He did not consider the question of specific interaction between solute and surface active agent, or between solute and solvent.

Both the LEWIS and the MAYERS correlation for the stirred cell are virtually independent of diffusivity, whereas the surface renewal theories of DANCKWERTS [41] and of TOOR and MARCHELLO [42], which would be expected to have some bearing on the surface clearing concept of MAYERS, involve the diffusivity to a power ranging from 0.5 to 1.0. The two correlations are somewhat "blanketting" - they cover a number of variables, but with less precision (± 40%) than is to be found among the experimental data themselves.

1.6 SHERWOOD and GORDON [6] obtained a correlation between mass transfer and diffusivity to the power 0.5 by running their stirred cell at a single speed, and using a single solvent system (water isobutanol). They assumed no resistance at the interface. Solutes were isobutanol, water, ammonia and 15 organic acids and bases, giving a thousandfold range of distribution coefficient, but only a twofold range of diffusion coefficient in each phase. No attempt is made to find statistically the "best" exponent of diffusivity, but the overall coefficient is found to hold with an average deviation of ±10%, (and next to none outside ±20%) over a thirtyfold range in mass transfer

coefficient. Taking their mean coefficient as $10^{-3}$ cm $sec^{-1}$, one would expect their correlation to detect an interfacial resistance greater than 200 sec $cm^{-1}$. LEWIS inferred the existence of a resistance to transfer of acetic acid, diethylamine and ammonia between water and isobutanol, but was not able to calculate its value, as the systems were subject to spontaneous interfacial stirring, which, it was suggested, neutralized the effects of the resistance, so that the measured mass transfer coefficients had normal values. The concentrations used by LEWIS were about 0.5 M, those of SHERWOOD and GORDON about 0.03 M, so that there is a possible concentration effect to be considered. The latter authors do not mention spontaneous interfacial agitation, and the only resistance they found was a 20% decrease in coefficient on addition of surface active agent. SHERWOOD and LEWIS have exchanged views on their work [7].

1.7 BOYE-CHRISTENSEN and TERJESEN [8], in the latest of a series of papers by TERJESEN and coworkers on the subject of interfacial barriers to mass transfer, came to the conclusion that the surface active agent produced its effect by modifying the fluid notion near the interface. They decided against an explanation in terms of specific interaction between solute and surface active agent,

because in their experiments on extraction from falling drops, similar results were obtained for the two chemically different solutes iodine and o-nitrophenol.

1.8 STERNLING and SCRIVEN [9] have given a full review and discussion of the phenomenon of spontaneous interfacial agitation, which is attributed to local changes in interfacial tension arising for the most part directly from infinitesimal local fluctuations of concentration during mass transfer. The authors present a simflified mathematical model in terms of conventional linearized stability theory, based on the growth of small roll cells at the interface. From their analysis, the authors conclude that their model is unstable with solute transfer, if not in one direction then in the other. Moreover, if kinematic viscosity and solute diffusivity are both lower in one phase, the system is unstable with transfer in either direction. Where interfacial tension decreases with solute concentration, as is usually the case in practice, instability arises whenever solute is being transferred out of the phase in which kinematic viscosity is higher, or out of the phase in which solute diffusivity is lower. The theoretical results also suggest the importance of variables such as the steepness of the concentration profile near the interface, which is related to the initial difference of solute concentration

and the magnitude of the surface viscosity. No account is taken of surface compressibility as such, nor of the effect of upsets in interfacial tension due to comparatively large scale convection currents. No direct comparison between theory and experiment is presented.

# CHAPTER TWO

## Apparatus

### 2.1 Introduction

The experimental investigations discussed in the foregoing literature survey were performed on one of three types of apparatus: diffusion cell, stirred cell, and single drop extractor.

The simplicity of the apparatus makes it relatively easy to form a mathematical model for the diffusion cell. However, this apparatus suffers from three disadvantages: long contact times, the tendency for a stagnant interface to attract impurities, and inability to yield information under dynamic conditions.

For the stirred cell there is at present no well-established theory whereby, given the physical properties and dimensions of the system, it would be possible to predict theoretical mass transfer coefficients accurate enough to compare with experimental results.

For the single drop extractor, there exist several mathematical models, all of which are mentioned in a paper by HANDLOS and BARON [10]. They also present their own correlation, which has a root mean square error of 30%. However, these models do not fully describe the behaviour of the drop, which can deviate from them in

several ways: by oscillation, by assuming non-spherical shapes, and by setting up interfacial tension gradients which partially or wholly prevent internal circulation and surface renewal, [11] , LINTON and SUTHERLAND [5.]

In the light of the preceding consideration, it seemed that effort could profitably be devoted to the development of apparatus which would conform to the following criteria:

(a) The behaviour of the apparatus should approximate closely to some theoretical model.

(b) Side-effects and end-effects should be small, so that any deviation from theoretical behaviour can with more certainty be attributed to interaction of the solute-solvent system studied.

(c) Provision should be made against the tendency of an ageing interface to collect surface active impurities which modify its behaviour.

(d) To facilitate investigations, the apparatus should be simple, flexible, stable, rapid and economical.

(e) Both as a check on performance of the apparatus, and as an aid in interpreting results, provision should be made for the optical inspection and recording of phenomena.

With the above ends in view, two forms of apparatus were developed - a wetted wall column and a horizontal

cocurrent contactor. Both afford means for the continuous co-current contact of two fluid phases for a measured time interval at an interface of constant dimensions under conditions of rectilinear laminar flow with a parabolic velocity profile having its maximum at the interface.

## The Wetted Wall Column

### 2.2 Literature Survey - Falling Film Contactors

The suitability of the wetted wall column for research into gas-liquid mass transfer has been widely recognized. Many papers have been written on the hydrodynamics of falling films [12 - 15], and on their use in gas absorption studies [16 - 21].

In particular, KRAMERS and coworkers, by recognising and carefully eliminating errors due to entry effect, waves and exit effect, produced results of high precision.

By contrast, studies of liquid-liquid systems in wetted wall columns have been far less numerous and rigorous. The pioneer work in this field was that of FALLAH, HUNTER and NASH [22] who studied the transfer of phenol between a film of water falling down the inside of a wetted wall tower and a countercurrent core of kerosene as the bulk liquid phase. They observed that the bulk liquid appeared to be in turbulent motion, even at film Reynolds numbers of 10. Similar apparatus was used by three subsequent pairs of workers [23, 24, 25]. All four groups presented empirical correlations, mainly as log-log plots of dimensionless groups. The extent of agreement is discussed in [25] and found insufficient for

any claim of generality.

It seemed that a major obstacle to theoretical analysis of the results from the above apparatus lay in eddy motion inside the bulk phase. Preliminary experiments with aluminium powder in the two phases showed that this eddy motion was a consequence of the shear caused by too great a difference between the mean velocities of the film and bulk phases respectively. As a result, a thin layer of the bulk liquid was dragged along with the film, while the rest of the bulk phase recirculated, in a manner similar to that in which a bulk of fluid is stirred when a jet expands into it. (A similar effect is referred to later in connection with the horizontal extractor -§2.13, fig 2.4a). This shear with its attendant vorticity would be eliminated if there were zero velocity gradient across the interface. One possibility would be to have a liquid core with zero velocity gradient [19], the velocity in the core being equal throughout to the velocity of the interface. This method was rejected in favour of one which required simpler experimental apparatus, and produced a more economical ratio of bulk liquid to film liquid flow rate.

## 2.3 Description of Wetted Wall Column

The apparatus is shown in figs 2.1, 2.2. The film liquid enters by the central conduit A, is distributed by

cap B, forms a film over the inner wall C of the annulus CD, and after separation at F is withdrawn through outlet valve G. The bulk liquid enters at H, is distributed by cap B, flows cocurrent with the film through the annulus CD, and leaves through the piezo-ring outlets to valve I. The column was supported on a clampstand fitted with levelling screws, which rested on a flat heavy base backed by foam rubber to damp out vibration.

## 2.4 Layout of Apparatus (Fig. 2.1)

Each phase was fed to the apparatus from a Mariotte bottle, through a thermostat bath and a capillary flow meter. Thermostat temperature was 25 ± 0.1°C, and room temperature 24 ± 2°C. The flowmeters had a range of interchangeable capillaries on ground glass spherical joints. Connections were made with glass and rigid polythene tubing, the latter kept short to minimise the effects of any impurities which might be leached into the solvents. Flexibility in the lines was achieved by having plenty of bends and swivel joints. Lubrication, where necessary, was done with water or a graphite-glycerine paste for the organic phase, and with ordinary petroleum jelly for the aqueous phase. Flow was controlled by means of "Exello" glass taps, lubricated with the solvent phase. Samples were collected in 100 ml ground glass stoppered flasks.

## 2.5 Experimental Procedure (Fig 2.2)

The operational procedure consisted of filling the column first with the film liquid and adjusting its flow-rate to the required value. The bulk liquid was then allowed to enter the column, displacing the film liquid except for the thin film flowing over the inner wall C. When the level of the film liquid reached F, the valve I was opened wide, allowing the bulk liquid to leave freely, and valve G was adjusted to keep the film liquid at F.

Most of the runs were performed with the heavier $CCl_4$ phase running downwards as the film phase. In order to keep the inner wall of the annulus wetted by the organic liquid, it was necessary to apply several coats of silicone varnish (Hopkins and Williams "MS1107" baking varnish and "Repelkote" air drying varnish). The possibility that minute amounts of incompletely polymerized constituents of the organic coating would be leached into the film phase and affect the interface was considered. However, it was concluded that such risks were small, because, owing to the continual renewal of the film phase, and the relative speeds at the wall and the interface, impurities would have little chance of diffusing from the wall to the interface before they were swept out of the apparatus. In the course of experiments

it became apparent that effects from such causes, on mass transfer coefficient and height of stagnant layer, were small compared to the effects of the measured variables.

The use of an organic film was convenient down to a Reynolds Number of four. However, with high solute concentrations or surface active agents in the water phase, it was found impossible to wet the inner wall of the annulus so as to maintain a continuous film with the organic phase. In these cases the inner wall was thoroughly degreased, while the outer wall was given a thin coating of Repelkote, rubbed down when dry with cottonwool to obtain uniformity. Then the whole column, as shown in Fig 2.2, was inverted. By this means the lighter aqueous phase was made to form a rising film on the inner wall, with $CCl_4$ now flowing upward as the bulk liquid. Since glass is naturally well wetted by water (the contact angle being zero) this arrangement formed a continuous film down to a Reynolds number of one.

Attempts with a stainless steel inner tube were abandoned after initial wetting difficulties.

High concentrations (0.05%) of the surface active agent "Nonidet P 40" (Shell Chemical Co.), an ethylene oxide-octyl phenol 8 - mer, surprisingly enough produced inferior wetting. When the two phases were placed in a clean glass tube, the contact angle between glass and

interface was about 90°. Thus neither phase was favoured, and small breaches in the film did not heal. This trouble was not experienced with "Teepol 530", (Shell Chemical Co.), a 27% wt. secondary alkyl sulphate solution in water; the water phase contact angle was acute, and wetting was easy down to a Reynolds number of one.

## 2.6. End Effects

### (a) Entry Effects:-

There are two effects: firstly, the acceleration of the film up to its final velocity profile; secondly, the initial drag of the film on the bulk. The first is negligible at low Reynolds number; the second is minimized by making the cap B (fig 2.2) thin, with free space above it, so that the bulk liquid enters the annulus CD with a shallow velocity profile at the edge of B [26]. Both effects were ignored in calculations.

### (b) Exit Effect:-

The height EF (fig 2.2) was kept equal to that of the stagnant end zone, noted by observing graphite particles deposited on the interface. Since practically no mass transfer occurs in this section [17, 18] the effective height of the column was thus BE.

## 2.7 Rippling of the Interface

In an attempt to provide a mathematical model for the

appearance of ripples, T. BROOKE BENJAMIN [12] considers an air-water interface wherein everpresent small vibrations are amplified exponentially along the length of the column. In agreement with his conclusions, many authors observed an initial height of column (about 10 cm) and a critical Reynolds number (about 20) below which waves had not yet grown large enough to be visible. The liquid-liquid system studied here seems to be more prone to rippling: waves were visible down to Re of 1, and there was no initial wave-free section of the column. Visual examination of the waves by stroboscopic light did not reveal any marked regularities in wave structure.

2.8 Velocity at Interface: For reasons stated elsewhere (§ 2.2) liquid flowrates were adjusted so as to maintain zero velocity gradient across the interface, in accordance with the equations given at the end of this section. However, the presence of waves tends to increase the interfacial velocity by increasing the thickness of the film at the crests of the waves, as was observed by Grimley [14] using an ultramicroscope technique. Therefore, in order to obtain the true velocity, it was necessary to time the interface. The method finally adopted was to suspend in the water phase small particles of oil-soluble blue dye having low surface activity

(Williams's "W.H.L. Dyestuffs, Oil Soluble Blue S.W.S.") It was possible by this means to locate the interface, because particles present there dissolved in the $CCl_4$ phase to produce easily visible blue spots. It was found that at Re of 8 the actual interfacial velocity was 25% greater than theoretical, the discrepancy decreasing to 3% at Re of 1. The presence of waves caused the particles at the interface to move in irregular paths, and timing was subject to a random deviation of $\pm 3\%$. The mean of twenty determinations was taken for each velocity.

2.9 } Flow Calculations. See Appendix 1.
.10 }

## Horizontal Cocurrent Contactor

### 2.11 Literature Survey

In the course of the investigation it became necessary to obtain schlieren photographs of the interfacial region, and also to obtain mass transfer coefficients for film thicknesses and contact times greater than those available with the wetted wall column. It was thought that some modification of the horizontal cocurrent contactor described by BHATTACHARYA [28] might achieve these aims, while still conforming to the criteria discussed in § 2.1. Previous workers [29]

reported a tendency for the interface to become stagnant and collect impurities. Bhattacharya demonstrated that this tendency was an end-effect caused by the flow divider on the exit end piece. At this end the interfacial layers necessarily came to a halt, and the surface pressure of accumulated impurities caused the stationary portion to propagate itself so as to cover slowly the whole length of the interface. Recently, Reid [49] has demonstrated that there is a maximum length the stationary portion can achieve. In the apparatus of Bhattacharya the interface was not allowed to come to rest at the exit end, nor was any attempt made to separate the phases in the apparatus, but instead both phases flowed together out to waste through the aperture of a special gate valve. Samples for analysis were taken through a hypodermic needle under isokinetic conditions. The vertical traverse of the needle could be accurately regulated relative to the interface by a micrometer screw. It is considered that this sampling technique is not only slow but a major source of possible errors, because it bases the calculation of overall mass transfer coefficient on samples drawn from a small area near the tip of the needle, which represents less than $\frac{1}{2}\%$ of the total cross sectional area of the apparatus, and which

lies in a region of steep concentration gradients; thus any random distortions in the streamlines near the needle could easily impair the representativeness of the sample.

2.12 Development of the Apparatus.

For the above reasons, means were sought whereby the two phases could be separated and analysed in order to obtain the total mass transfer rate in the apparatus. The chief obstacle to separation is the tendency for the interface to become stagnant. An attempt was made to divide the stagnant section from the moving section, as in the wetted wall column. Accordingly, the interface at the exit end of the horizontal apparatus was allowed to flow over a weir and to run in a narrow film down a height of 5 - 10 cm before the two phases were separated. However, this did not prevent the horizontal interface from coming to rest, presumably because pressure gradients in the horizontal section are so small that they are unable to overcome even a moderate back pressure from the accumulated interfacial agents at the exit end. Means were therefore provided to clean the interface by allowing one of the liquids, after falling over the weir and running down a height of 5 cm, to separate from the tip of the weir in the form of droplets, which carried away on their surface the accumulated interfacial impurities

A similar method was used by Pigford and Wendel [20] who eliminated the stagnant exit section of a wetted wall column by allowing a periodic overspill to flush off impurities.

Another problem was to obtain a parabolic velocity profile with a maximum at the interface, which proved unexpectedly difficult. The profile was observed experimentally by injecting into the streams dyes of low surface activity: water soluble Congo Red, and "Oil Soluble Blue S.W.S" (Williams of Hounslow, Ltd.). Interfacial velocities were determined by timing graphite particles deposited on the interface. After a number of experiments it was concluded that the velocity profile depended critically on the shape and size of the exit weir and also on concentration of solute in both phases. No correlation was found between interfacial velocity and bulk fluid velocity, nor was a design of weir found which would make possible the desired velocity profile except over a very narrow range of flowrates and inlet concentrations. The weir shape finally adopted is shown in fig 2.3. A range of these weirs were made, with throat dimension T from 0.1 cm to 0.5 cm corresponding to volume flowrates from 0.01 to 1.0 cc/sec. To each throat dimension there corresponded a narrow range of flowrate at which the

desired velocity profile was obtained. For lower flowrates, the profile was as in fig. 2.4a. Capillary action at the weir sucked the interface forward at a velocity much greater than the mean bulk velocity. Hence the velocity profile became inverted, and the bulk flow split up into a narrower, faster forward moving interfacial zone, and a compensatory wider, slower backward moving zone.

Weirs without the narrower throat section, T, tended to give excessively inverted profiles for reasons connected with the shape of the interface as the discharge fell over the crest of the weir.

For volume flowrates higher than the critical, the reverse occurred: the profile became W shaped (Fig 2.4c) with the interfacial velocity slower than the mean bulk velocity.

2.13 Description of Apparatus. (Fig. 2.3)

The working section consisted of a rectangular channel 1" broad, about $\frac{1}{2}$" deep and 11" long, made by gasketting plate glass walls between flat sections of stainless steel. A gasket material found to have a usable combination of compressibility and solvent resistance was "Uniphase" resin bonded cork (Armstrong Cork Co. Ltd.). Cracks were stuffed with asbestos paper.

The weir was made of glass sections ground to shape

on a wheel and cemented with "Araldite" epoxy resin ("C.I.B.A. (A.R.L) Ltd."). The resin tended to lose its bond strength when immersed in the solvents. The weir was sealed into place with "Polyfilla" ("Polycell Products, Ltd."), a cement resembling plaster of Paris, which was solvent resistant. The main virtue of this method of fabrication was adaptability to a variety of weir designs.

In order to make the organic phase wet the weir, the latter was given several coats of a silicone baking compound (Hopkins and Williams "M.S.1107"). The coating needed periodic renewal. Low density polythene was very well wetted by the organic phase, but was not dimensionally stable. Aluminium was well wetted by the aqueous phase but tended to corrode. Teflon and non-porous impervious graphite were not well wetted by either phase.

The long tip of the weir (5 - 10 cm) projected into the outlet tube A. The liquid which wetted the weir ran along the tip, which was completely immersed in the non-wetting liquid and detached itself from the tip in the form of drops. The drops were coalesced a short distance above their point of formation, and this phase then flowed through the outlet valve G. The liquid which did not wet the weir was withdrawn through an outlet tube near the weir but upstream of the mask M.

The purpose of the mask M was to separate the main stream of non-wetting liquid from the blanketting volume of non-wetting liquid which surrounded the drops in outlet tube A. The mask was adjusted so that it permitted the minimum of mixing between the two sections, but did not interfere with the free flow of the interface. As a result, the solute concentration of the continuous phase surrounding the drops eventually came to equilibrium with that of the incoming dispersed phase, thus considerably reducing the driving force for mass transfer in the exit section. In order to estimate the amount of mixing between the two sections, dye was introduced into the continuous phase of the separation chamber A, and the time taken for the colour to become diluted to a matched standard was noted. (In the absence of a mask adjustable from outside repeated adjustment of the mask was a laborious procedure which involved emptying the apparatus and removing the end closure B.)

The tongue C served to separate the two phases at the upstream end of the channel. By using tongues of different length, the length of the channel could be varied. (As the channel used was already rather short in relation to its depth, not much variation in length was permissable in this case; only two tongues were used.)

2.14 Method of Operation.

Originally the apparatus was run with the heavier $CCl_4$ phase wetting the weir, and falling as drops through the water phase. However, the silicone coating on the glass weir needed frequent renewal; hence it was decided to degrease the weir and make water the wetting phase. To this end, the apparatus was inverted. Water then rose up through the $CCl_4$ phase which now filled the outlet tube surrounding the weir. Under these conditions the method of operation was as follows:

The apparatus was filled with the water phase, air bubbles being sucked out through the hypodermic needles N. The bottom half of the channel and the outlet tube A surrounding the tip of the weir were then filled with the $CCl_4$ phase. Inlet and outlet flowrates were then adjusted to obtain the required velocity profile, and to keep the meniscus in the outlet tube A at a constant level above the tip of the weir. Any change in this level would cause mixing between bulk ( $CCl_4$ ) phase from the mainstream and masked sections, which could upset analyses of the outlet bulk phase; for this reason exit concentrations of the dispersed (water) phase tended to be the more reliable as they were comparatively insensitive to small changes in concentration of the masked bulk phase.

In order to measure interfacial velocity, graphite particles were injected onto the interface and timed. Assuming parabolic velocity profile in the plane of the interface, the average interfacial velocity could be taken as two thirds of the measured velocity of particles at the centre of the interface.

After liquid had flowed through the apparatus equivalent to ten times its holdup, samples were taken at intervals of one holdup volume and analysed until constant values were obtained.

2.15 End Effects. Both end effects were neglected in mass transfer calculations.

(a) Entry Effect. When the apparatus was working properly, it was found that the interface reached its final velocity within one or two film thicknesses. Because of the low flowrates used, entry turbulence was negligible.

(b) Exit Effect. Because of the increased surface area and turbulence in the drop forming section, there is a possible large exit error. Bhattacharya [28] found that in his experimental set-up mass transfer during formation and coalescence of drops produced about 15% extraction. However, the presence of the mask greatly reduces the driving force for mass transfer in the masked bulk phase. If the mask were perfect, the masked bulk

phase would in time reach equilibrium with the entering dispersed phase. However, some leakage takes place. In order to estimate this leakage, it was noted that dye injected into the masked bulk phase took one hour to reach one tenth its initial concentration. Hence it was estimated that masked bulk phase was being replaced by fresh liquid from the mainstream bulk phase at a rate of 0.1% of the masked volume per second, and that the resultant error in mass transfer was about +5%.

2.16 Photographic Investigations.

In order to observe eddy currents in the apparatus, it was placed in a schlieren set-up [30]. The method consisted in passing a beam of monochromatic light through the liquid phases and then bringing the image into point focus just touching a knife edge. Local variations of refractive index in the liquids were thrown out of focus and consequently could be stopped by the knife-edge, so that they showed up as dark regions when the image was projected onto a screen. Because of the curvature of the meniscus, the interfacial region could not be observed. Some reduction in curvature was achieved by careful application of a thin silicone film ("Repelkote") to the glass walls of the apparatus (cf. [1]). It was also possible to take shadowgraphs

cast by eddies near the interface, but this method is less sensitive than the schlieren method (Plate 5.7)

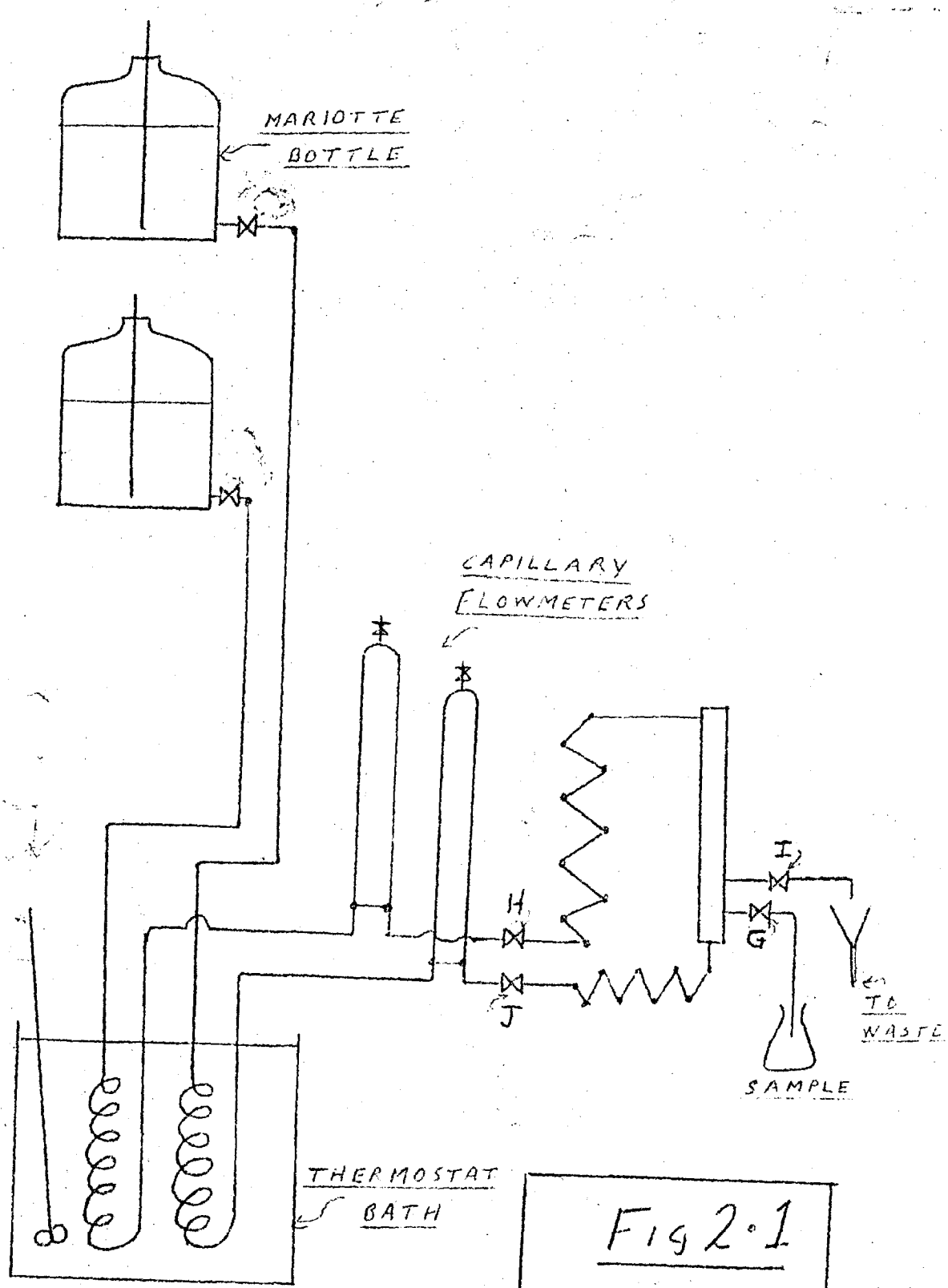



Fig 2·1

LAYOUT

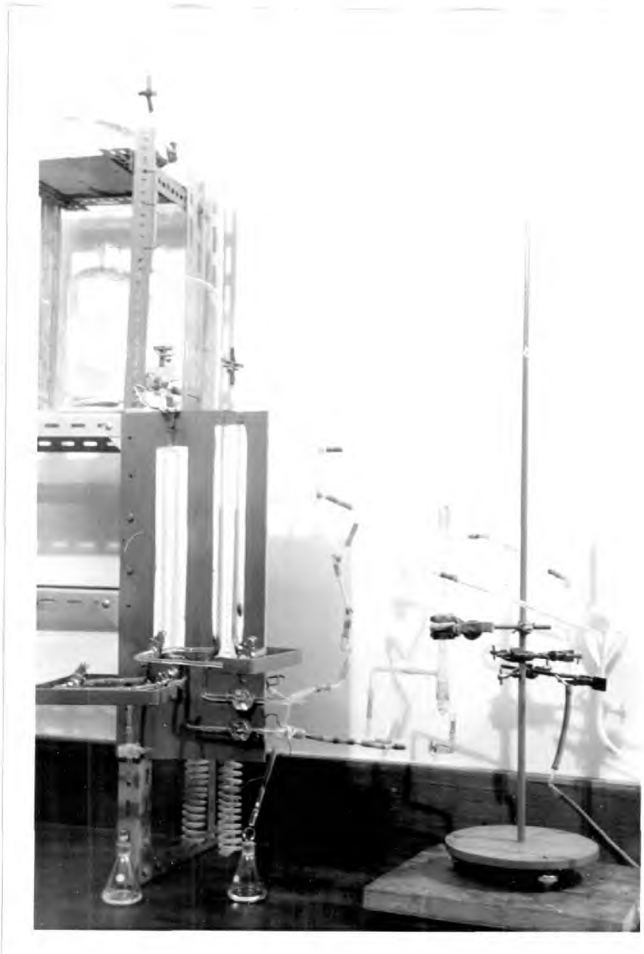


PLATE 2.1 - VERTICAL CONTACTOR

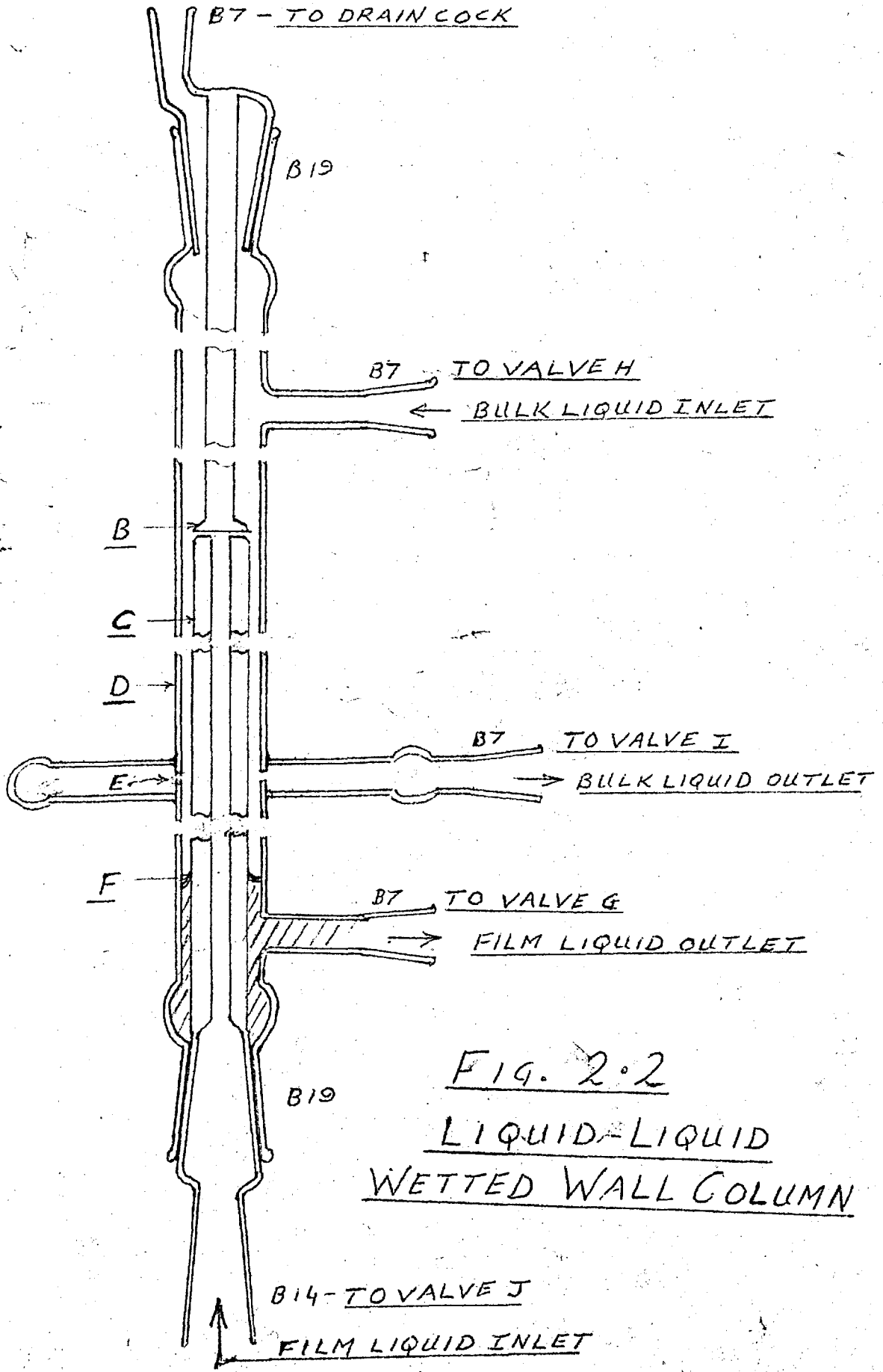



FIG. 2.2

LIQUID-LIQUID WETTED WALL COLUMN

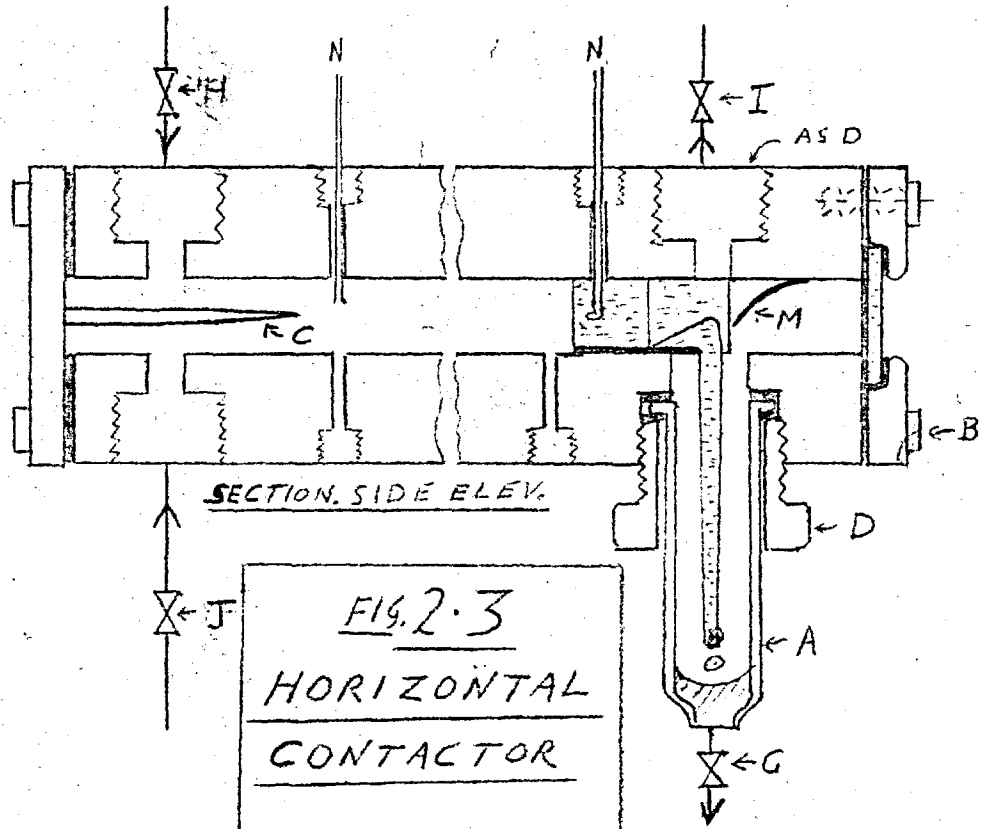
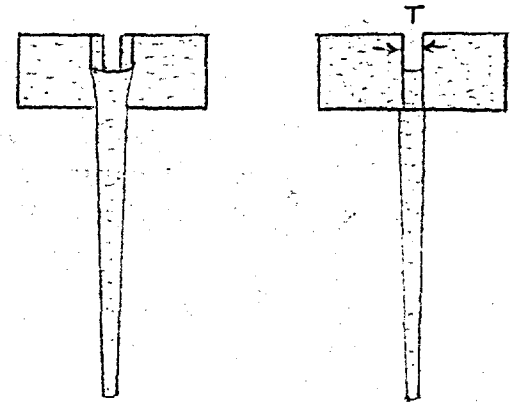
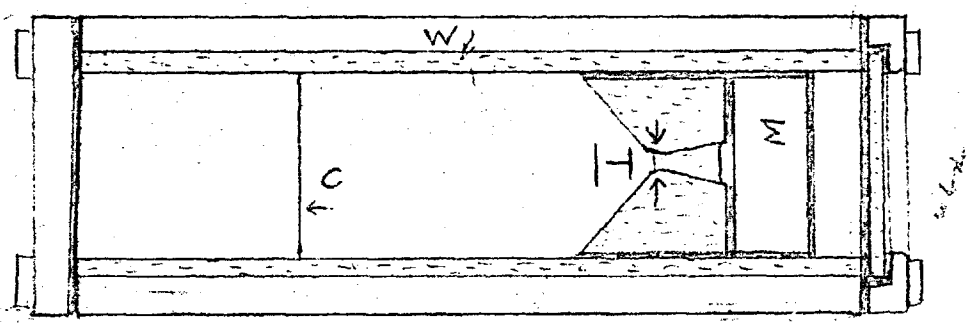



FIG. 2·3
HORIZONTAL
CONTACTOR

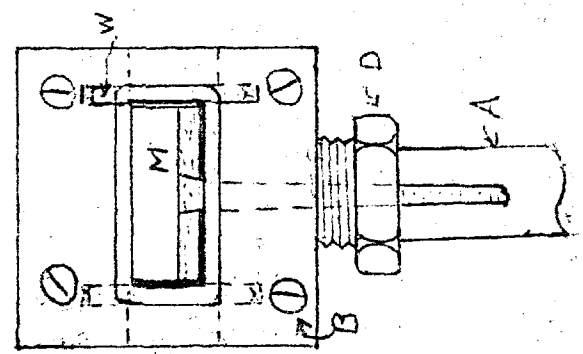



FRONT VIEW OF WEIR

REAR




PLAN




END ELEV.

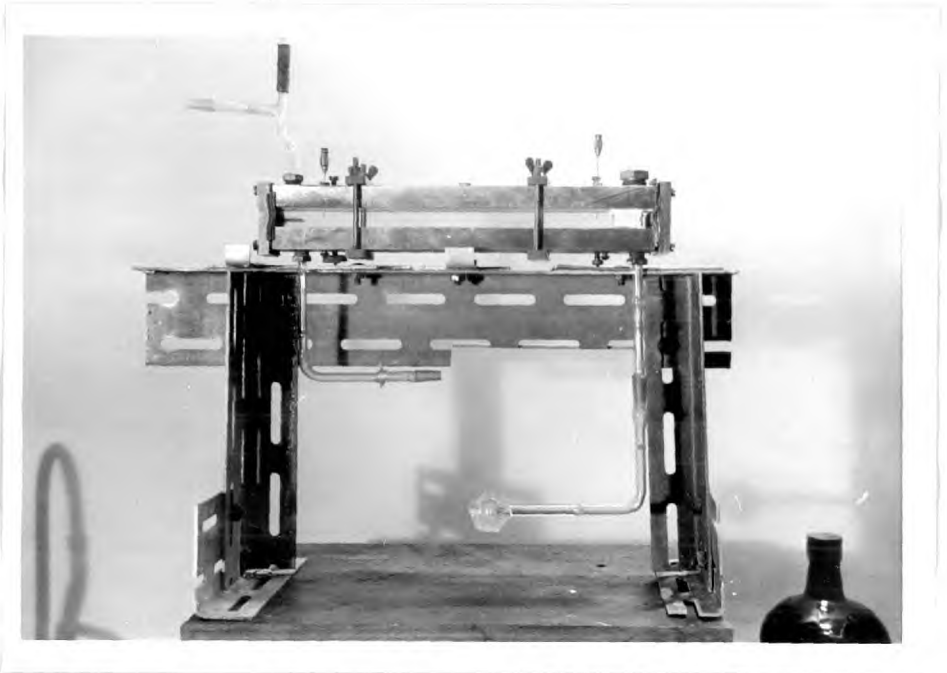
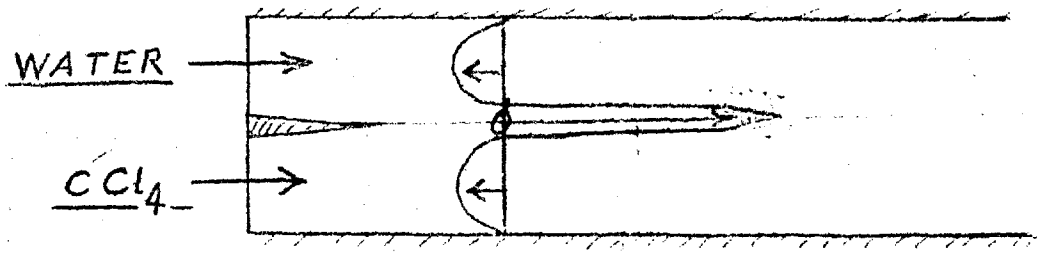
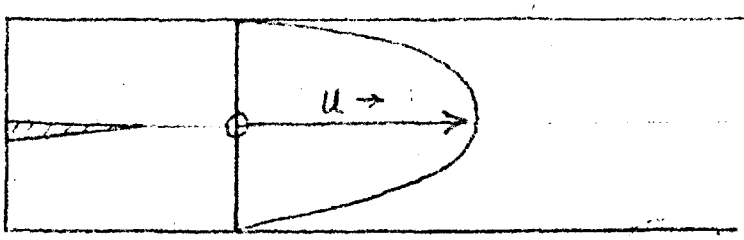


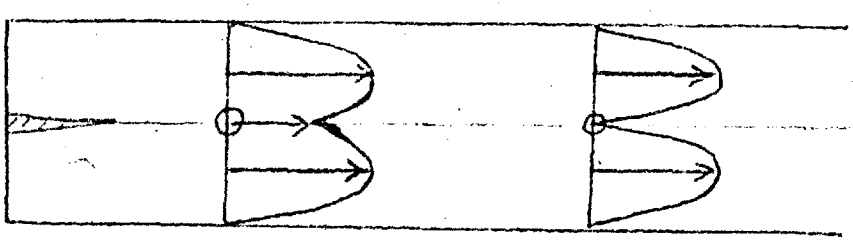
PLATE 2.2 - HORIZONTAL CONTACTOR




(a) INVERTED




(b) SINGLE



(c) DOUBLE

FIG. 2.4 - VELOCITY PROFILES IN THE HORIZONTAL CONTACTOR

# CHAPTER THREE - Equilibrium Data

## 3.1 Distribution Coefficient

A review of published equilibrium data for quaternary liquid-liquid systems showed them to be concerned with solute concentrations high enough to cause appreciable changes in solvent miscibility, in activity and in diffusion coefficient. Also, the majority of these data were obtained by the synthetic method (e.g. "cloud point" titrations) and the solutes were not readily analysable for concentration.

3.2. Choice of System: In order to avoid the above complications, new distribution data were needed. A first choice, later rejected, was $CCl_4$ - $H_2O$ - $I_2$ - Phenol. Transfer of iodine between $CCl_4$ and water had been studied by Terjesen and coworkers [8]; and phenol could be estimated with the same chemical reagents as for iodine. Ternary distribution data were soon obtained, but despite several days agitation of the solutions in a thermostat bath, no consistent distribution coefficients could be found for the quaternary system This lack of equilibrium was attributed to a very slow reaction between iodine and phenol, which led to the formation of a white film at the interface, although no reference was found in the literature to such a

reaction. Accordingly, iodine was abandoned as a solute because of its possible reactivity, although it offerred interesting features, firstly in not being surface active, secondly in having a rather one-sided distribution coefficient which could be varied by the addition of phenol.

The system $CCl_4$ - $H_2O$ - Phenol - Propionic Acid was finally chosen. Blokker [5] and Lewis [3] reported a resistance to extraction of propionic and other carboxylic acids from toluene into water. They attributed this resistance to dimerization in the aprotic solvent. Since propionic acid is dimerized in $CCl_4$ to a much larger extent than is phenol, it was thought that simultaneous transfer of the two solutes would provide an interesting comparison.

3.3 Determination of Solute Concentration.

Chemical analysis was chosen because it provided a specific estimate of each solute without great capital outlay.

(a) Phenol. The bromine method was used [47]. Accurately $^N/_{10}$ brominating solution was prepared by dissolving 2.784 gm potassium bromate and 15 gm potassium bromide per litre with distilled water. An aliquot of sample (either water or $CCl_4$ phase)

estimated to contain the equivalent of 15 ml 0.1N solution was pipetted into a 500 ml ground-glass stoppered titration flask containing 50 ml water and 25.00 ml brominating solution (sufficient to give at least 2% stoichiometric excess of bromine.) The solution was brought to 25°C and hydrochloric acid added to make 0.8N HCl. The flask was stoppered and shaken well for one minute to promote diffusional mixing. Excess bromine was removed by adding one gram of KI in the form of 20% solution, taking care, by first moistening the lip and stopper, and opening slowly, not to let any bromine vapour escape. The stopper was washed down with distilled water into the flask and replaced. The flask was shaken for another minute. The liberated iodine was titrated with N/10 solium thiosulphate, using starch or sodium starch glycollate as indicator. A blank was run and used to standardise the thiosulphate solution. Normality of Thiosulphate solution x Difference between the two titrations = $^1/_6$ (Molarity of Phenol).

(b) Propionic Acid was estimated by direct titration with N/5 or N/40 Barium Hydroxide Solution, using neutralized Phenolphthalein indicator. Solutions were warmed to 50°C before titrating, and were brought to boiling near the endpoint, to expel any

dissolved carbon dioxide. For the $CCl_4$ phase, an aliquot was placed in a 150 ml. conical flask together with 10 - 20 ml $Co_2$ - free water to extract the acid, and titrated as above. The endpoint was taken as the first permanent pink colour in the water phase. With the more dilute solutions, colour at end point was estimated by comparison with a blank sample against a white tile background.

The barium hydroxide solution was stored in a 3l. aspirator fitted with a $CO_2$-absorbing vent to atmosphere. Solution was led by tubing from the aspirator to easy-fill type burettes, and the air space in the top of the burettes was connected back by tubing to the air space in the top of the aspirator, to maintain a closed $CO_2$-free system.

Glassware. Burettes and pipettes were calibrated to Grade A standard. In order to avoid sucking the toxic $CCl_4$ phase by mouth, a plunger-type pipette was used, or alternatively, a plastic squeeze-bottle with a rubber tube fitting smoothly over the mouth of an ordinary pipette.

Reagents. Hopkins and Williams Ltd.: "Analar" phenol; "Purified" propionic acid; "Analar" $CCl_4$, (recovered after use by water washing and distillation - no difference was detected in distribution coefficient.)

3.4 Experimental. A wire cage was constructed to hold 6 glass-stoppered conical flasks (100 ml) totally enclosed in a 25°C ± 0.1°C thermostat bath, while rocking them in a short arc up to 400 cycles per minute. The reagents were placed in the flasks in quantities estimated to give a set of points over a variable range of propionic acid concentration; the concentration of phenol as a parameter was kept constant in the $CCl_4$ phase. The mouths of the glass-stoppered flasks were then waterproofed by covering with a polythene sheet and rubber bands, and the flasks were shaken in the cage at a speed great enough to disperse the two phases in one another. After shaking, the phases were allowed to settle for one hour, and samples were analysed. The shaking and sampling procedure was repeated until no further concentration changes were detectable. Except for the phenol-iodine system mentioned at the beginning of this chapter, overnight shaking was sufficient to produce equilibrium.

## 3.5 Results and Discussion

### Nomenclature

The distribution coefficient m is defined by

$$m_A = C_{C,A}/C_{W,A} \qquad (3\text{-}1)$$

where $C_A$ is the molarity (mole per litre) of solute A,

and subscripts C and W refer to the carbon tetrachloride and aqueous phases respectively. Numerical values are given in Tables 3.1 to 3.3.

Phenol

Graph 3.1 shows results for the distribution coefficient of phenol alone, compared with results from two other sources [31, 32]. It can be seen that the present set of data fall between the other two and have less scatter. They are represented within experimental error (0.4% r.m.s.) over the concentration range $0.01 \quad C_{C,Ph} \quad 0.22$ by the straight line

$$m_{Ph} = 0.400 + 1.78\ C_{C,Ph} \qquad (3\text{-}2)$$

According to E.G. HOFFMAN (1943), quoted in [33], phenol exists in carbon tetrachloride solution almost completely in monomeric form at low concentrations, but as its mole fraction increases, hydrogen bonding takes place between pairs of phenol molecules to a rapidly increasing extent. At 0.2 Molar phenol about 5% of the phenol molecules are dimerized, while at 1 M the proportion rises to 70%.

Propionic Acid. Graph 3.2 shows $m_{pr}$ for propionic acid without phenol, together with data from [31]. In the range $0.01 \quad C_{C,Pr} \quad 0.23$, the following relationship holds within 0.3% r.m.s.:

$$m_{Pr} = 0.638 \quad C_{C,Pr}^{0.474} \qquad (3\text{-}3)$$

If dimerization were complete, the exponent would be 0.5. However, the dielectric properties of the solvent tend to break the hydrogen bonds, thus decreasing the dimerization. The dimerization constant and the percentage dimerization were estimated from the distribution coefficient [34] and found to be about 470 and 90% respectively, at $C_{C,Pr} = 0.1$.

The percentage dimerization in the aqueous phase was estimated using a value of 20 for the dimerization constant quoted by Davies [35], and found to be 0.3% at $C_{W,Pr} = 0.1$.

The percentage ionization in aqueous phase, estimated from the ionization constant, was 1% at $C_{W,Pr} = 0.1$, and 3% at $C_{W,Pr} = 0.01$. Thus about 98% of propionic acid in the aqueous phase exists as unionized monomer.

Phenol + Propionic Acid. The combined solutes have a mutual effect of increasing the distribution coefficient so that solubility in the $CCl_4$ phase is relatively increased. It was thought that this tendency might be due to hydrogen bonding between phenol and propionic acid in the $CCl_4$ phase, with activities in the aqueous phase being relatively little changed. (Dipole moments: $H_2O$ 1.85, Propionic Acid Monomer 1.75, Phenol 1.4, Propionic Acid dimer 0.6, $CCl_4$ 0.) Therefore

attempts were made to correlate distribution coefficient with concentration in $CCl_4$ phase. To this end, graphs were constructed of $m_{Pr}$ vs. $C_{C,Pr}$ for various levels of $C_{C,Ph}$; and hence of $m_{Pr}$ vs $C_{C,Ph}$ at various levels of $C_{C,Pr}$. Similar graphs were drawn, mutatis mutandis, for $m_{Ph}$. Each solute showed linear increase in m with concentration of the other solute:

$$m_{Pr} = 0.638\ C_{C,Pr}^{0.474} + 0.30\ C_{C,Ph} \qquad 3\text{-}4$$

$$m_{Ph} = 0.400 + 1.78\ C_{C,Ph} + 0.44 C_{C,Pr} \qquad 3\text{-}5$$

Tables (3.1,.2,.3) show the extent of agreement between experimental values of m and values calculated from equations (3-4,-5). On the whole, the correlations are "good", i.e. the agreement is within experimental error.

Discussion of Errors. Routine acid-base titrations with Grade A burettes and 20 ml pipettes should have an accuracy of 0.2%. The actual r.m.s. scatter of the propionic acid equilibrium values is 0.22% (Table 3.2). The phenol determinations have a greater error (0.4-0.8%) for two reasons: firstly the tendency of bromine and phenol to produce side reactions unless conditions are very carefully controlled; secondly, the low equivalent weight of phenol in this method made it necessary to pipette smaller samples (down to 1 ml.), with concomitantly greater chances of error.

Table 3.1:- Propionic Acid

| $C_{C,Pr}$ Expt. | $C_{C,Ph}$ Expt. | $m_{Pr}$ Expt. | $m_{Pr}$ Calcd. | % error |
|---|---|---|---|---|
| 0.0100 | 0 | 0.0740 | 0.0747 | -0.4 |
| 0.0220 | 0 | 0.1060 | 0.1045 | -1.4 |
| 0.0400 | 0 | 0.1400 | 0.1395 | -0.4 |
| 0.0693 | 0 | 0.1790 | 0.1800 | +0.6 |
| 0.1040 | 0 | 0.2160 | 0.2190 | +1.5 |
| 0.1200 | 0 | 0.2350 | 0.2340 | -0.4 |
| 0.1970 | 0 | 0.2920 | 0.2964 | +0.7 |
| 0.1850 | 0 | 0.2814 | 0.2870 | +0.2 |
| 0.2080 | 0 | 0.3020 | 0.3040 | +0.7 |
| 0.2200 | 0 | 0.3120 | 0.3110 | -0.3 |
| Arithmetical Mean Error | | | | +0.07 |
| Root Mean Square Error | | | | 0.22 |

Table 3.2:- Phenol

| $C_{C,Pr}$ Expt. | $C_{C,Ph}$ Expt. | $m_{Ph}$ Expt. | $m_{Ph}$ Calcd. | % Error |
|---|---|---|---|---|
| 0 | 0.0100 | 0.420 | 0.418 | -0.48 |
| 0 | 0.0390 | 0.450 | 0.470 | +2.3 |
| 0 | 0.0675 | 0.520 | 0.521 | +0.19 |
| 0 | 0.211 | 0.776 | 0.776 | 0 |
| 0 | 0.363 | 1.056 | 1.047 | -0.86 |
| 0 | 0.408 | 1.130 | 1.130 | 0 |
| Arithmetic Mean Error | | | | +0.15 |
| Root Mean Square Error | | | | 0.42 |

Table 3.3:- Propionic Acid + Phenol

| $C_{C,Pr}$ Expt. | $C_{C,Ph}$ Expt. | $m_{Pr}$ Expt. | $m_{Pr}$ Calcd. | % Error | $m_{Ph}$ Expt. | $m_{Ph}$ Calcd. | % Error |
|---|---|---|---|---|---|---|---|
| 0.00948 | 0.02998 | 0.08005 | 0.0791 | -1.3 | 0.4803 | 0.454 | -5.4 |
| 0.00866 | 0.03239 | 0.07694 | 0.0772 | +0.4 | 0.4348 | 0.464 | +6.5 |
| 0.00900 | 0.0800 | 0.09540 | 0.0940 | -1.6 | 0.5470 | 0.546 | -0.2 |
| 0.148 | 0.018 | 0.2585 | 0.259 | +0.2 | 0.510 | 0.497 | -0.6 |
| 0.1223 | 0.0166 | 0.2364 | 0.239 | +1.1 | 0.506 | 0.484 | -4.1 |
| 0.0784 | 0.1908 | 0.2454 | 0.247 | +0.7 | 0.7729 | 0.774 | +0.1 |
| 0.2221 | 0.08448 | 0.3301 | 0.335 | +1.5 | 0.652 | 0.648 | -0.6 |
| 0.1533 | 0.08337 | 0.2808 | 0.282 | +0.4 | 0.6199 | 0.606 | -2.3 |
| 0.1079 | 0.0763 | 0.2401 | 0.244 | +1.7 | 0.5786 | 0.578 | -0.1 |
| 0.03457 | 0.07267 | 0.1480 | 0.153 | +0.3 | 0.5238 | 0.545 | +3.9 |
| 0.03598 | 0.2075 | 0.193 | 0.195 | +1.0 | - | - | - |
| 0.01226 | 0.1898 | 0.1389 | 0.137 | -1.4 | 0.7379 | 0.740 | +0.3 |
| 0.160 | 0.4195 | 0.392 | 0.390 | -0.5 | 1.20 | 1.19 | -0.8 |
| 0.0745 | 0.4060 | 0.310 | 0.307 | -1.0 | 1.15 | 1.15 | 0 |
| 0.250 | 0.401 | 0.450 | 0.452 | +0.4 | 1.20 | 1.22 | +1.7 |
| Arithmetical Mean Error | | | | +0.15 | | | +0.07 |
| Root Mean Square Error | | | | 0.25 | | | 0.75 |

3.6 Interfacial Tension.

The variation of interfacial tension with concentration of solute during transfer was found to produce spontaneous interfacial disturbances which influenced coefficients of mass transfer. As an aid in interpreting these effects equilibrium interfacial tensions were measured.

3.7 Experimental. The drop weight volume method was employed [36].

All parts of the apparatus likely to come into contact with the solutions were degreased with hot chromic acid mixture. Cleanliness of surfaces was tested by observing whether they could support an unbroken thin film of water. The water used was freshly distilled; [37] observed that de-ionized water contained traces of surface active degradation products from the cation-exchange resin. Reagents were Hopkins and Williams "Analar" grade phenol and carbon tetrachloride, and "Purified" grade propionic acid. The liquid reagents were redistilled and the middle fractions were used.

Solutions were prepared and shaken to equilibrium as described previously for Distribution Coefficient. (In fact some distribution coefficients were determined on the same runs.) Aqueous phase was then sucked into

the rising drop pipette, first rinsing and then filling up to the top of the bulb. The mouth of the pipette was then closed and carbon tetrachloride phase was poured into the reservoir surrounding the tip. The procedure adopted was then as described by Harkins [36] except for the following modifications:

(a) Instead of controlling the drops by sucking or blowing orally, 2ft of rubber tubing was attached to the mouth of the pipette, having several screw clips along its length. By screwing or unscrewing successive clips, air could be pushed into or sucked out of the pipette at a more easily controlled rate.

(b) To reduce vibration the thermostat stirrer was switched off shortly before each drop was due to detach.

3.8 Results and Discussion. Data for interfacial tension are presented in Table 5 and Graphs 3 and 4. Density data for the drop weight volume method are presented in Graph 5. The interfacial tension between the pure (i.e. solute-free) solvents $\sigma_o$ was found to be 44.7 dynes/cm $\pm$ 1%. The same value was found using both "Analar" $CCl_4$ and $CCl_4$ recovered by washing with water and redistilling. It compares with a value of 44.6 $\pm$ 1% taken from fig. 9 in [36], but is 2% higher than the value of 43.7 obtained with the pendent drop method by Donahue and Bartell [38].

The presence of a solute which is positively adsorbed at the interface decreases the interfacial tension. This lowering

$$\Delta\sigma = (\sigma_o - \sigma)$$

is known as the Surface Pressure.

Propionic Acid. Graph 3.3 shows $\Delta\sigma$ vs. concentration in the water phase $C_{W,Pr}$ for the system propionic acid-water-$CCl_4$. The data shown are only 2% higher than the equivalent data of TAMAMUSHI 39 for surface tension of propionic acid -water-air. The close agreement between these values suggests that propionic acid molecules in the $CCl_4$ phase do not contribute as much to the lowering of interfacial tension as do those in the water phase. According to HARKINS, 36 pp. 30-36, the solute at an interface tends to form a bridge between the intermolecular force fields of the two phases, in such a way that the transition between them is made more gradual: "If at an interface the transition from liquid A to liquid B is made by a saturated film of solute molecules which.....have one end like A and the other end like B, then the free surface energy is greatly reduced". Since interfacial tension is a direct measure of interfacial free energy, it follows from this view that interaction between carbon tetrachloride and propionic acid molecules does not

contribute much to the total decrease in free energy caused by addition of propionic acid to the water - $CCl_4$ interface.

Phenol. By contrast with the behaviour of propionic acid above, the lowering of surface tension produced by phenol in the phenol-water-air system, 32 is about half of that in the phenol-water-$CCl_4$ system shown in Graph 3.3. According to the view of Harkins this additional lowering of interfacial free energy must be due to interaction between $CCl_4$ and the phenyl radical making the transition from the molecular interactions of $CCl_4$ to those of water more gradual.

Propionic Acid - Phenol - Water - $CCl_4$.

The following graphical procedure was used to correlate the experimental quaternary data in Table 3.4 with the ternary data in Graph 3.3. Let the concentration of phenol and propionic acid in the water phase be $C_{W,Ph}$ and $C_{W,Pr}$. From Graph 3.3 or table 3.4 the value of $\Delta\sigma^1$ was read at $C_{W,Pr}$, and the "equivalent phenol concentration" $C_{W,Ph}{}^1$ was read at $\Delta\sigma^1$. Then $C_{W,Ph}{}^1$ was added to the actual phenol concentration $C_{W,Ph}$ to obtain the "total equivalent phenol concentration" $C_{W,Ph}{}^1 + C_{W,Ph}$, and the calculated value of $\Delta\sigma$ was read at this concentration from Graph 3.3. From Table 3.4 it is seen that the correlation predicts about

2% too low, but this was considered acceptable compared with experimental error (±2%).

Consideration of Errors. From consideration of values for $\sigma_o$, errors due to chemical impurities are thought to be less than those due to experimental limitations. Errors in drop volume varied from 0.7% to 2.0%, increasing as drop size decreased. Error in density determination was 0.2%. Errors in concentration determination were 0.3% for acid, 0.6% for phenol. The average total error was thus about 2%

Table 3.4 - Interfacial Tensions.

| $C_{C,Pr}$ | $C_{W,Pr}$ | $C_{C,Ph}$ | $C_{W,Ph}$ | $\sigma$ Exptl. | $\sigma$ Calcd. | % Error |
|---|---|---|---|---|---|---|
| 0.00688 | 0.113 | 0 | 0 | 37.2 | | |
| 0.0260 | 0.225 | 0 | 0 | 32.6 | | |
| 0.0408 | 0.289 | 0 | 0 | 30.8 | | |
| 0.0874 | 0.432 | 0 | 0 | 27.2 | | |
| 0.208 | 0.686 | 0 | 0 | 23.4 | | |
| 0 | 0 | 0.0083 | 0.0185 | 37.2 | | |
| 0 | 0 | 0.0164 | 0.0383 | 30.9 | | |
| 0 | 0 | 0.0716 | 0.136 | 22.0 | | |
| 0 | 0 | 0.0724 | 0.137 | 21.6 | | |
| 0 | 0 | 0.183 | 0.246 | 13.9 | | |
| 0 | 0 | 0.368 | 0.430 | 8.8 | | |
| 0.0090 | 0.0945 | 0.0800 | 0.146 | 19.0 | 19.7 | +3 |
| 0.0251 | 0.186 | 0.0771 | 0.143 | 18.4 | 19.0 | +3 |
| 0.0739 | 0.288 | 0.231 | 0.282 | 11.0 | 10.7 | -3 |
| 0.256 | 0.713 | 0.074 | 0.116 | 14.3 | 14.2 | -1 |
| 0.164 | 0.580 | 0.0745 | 0.123 | 15.0 | 14.7 | -3 |
| 0.125 | 0.490 | 0.0675 | 0.114 | 17.1 | 17.2 | +1 |
| 0.077 | 0.380 | 0.070 | 0.127 | 18.1 | 18.1 | 0 |
| 0.0169 | 0.153 | 0.065 | 0.120 | 20.8 | 21.2 | +2 |

3.9 Interfacial Excess of Solute.

The number of solute molecules adsorbed at the interface was estimated from the Gibbs adsorption isotherm:

$$\Gamma = \frac{N_A}{RT} \cdot \frac{d\sigma}{d(\ln a)} \qquad (3\text{-}6$$

$\Gamma$ is the interfacial excess of solute, i.e. the total number of solute molecules in the interfacial zone, less the number that would be there if the bulk concentration C were to extend unchanged up to the interface. $N_A$ is the Avogadro number, a is the activity of the solute.

Assuming activity to be proportional to concentration, and substituting numerical values for $N_A$, R, T, the following form of equation (3-6) was used:

$$\Gamma = 2.42 \times 10^{13} C_W \cdot \frac{d\sigma}{dC_W} \text{ molecules/cm}^2 \qquad (3\text{-}7)$$

Concentration $C_W$ was used rather than $C_c$; firstly, because variation of activity coefficient was smaller in the water phase, secondly in order to compare more readily with surface tension data in the literature. Since $C_c = mC_W$, then, provided m is approximately constant, equation (3-7) shows that the same value of should be obtained for either phase.

## Individual Solutes

Some picture of the distribution of the molecules at the interface may be obtained from table 3.5, which shows the effect of interfacial tension on the molecular concentration and free area of solute at the interface.

Table 3.5: Interfacial Films of Single Solutes

| Solute | $C_W$ | Interfacial Pressure | Molecules adsorbed ($\Gamma$) x $10^{-13}$ | per sq. cm. Already Present x $10^{-13}$ | Area per Molecule (Sq. Angstrom) | Available Area Ratio |
|---|---|---|---|---|---|---|
| Propionic Acid | 0.01 | 0.4 | 1.5 | 0.06 | 640 | 26 |
| | 0.10 | 4.0 | 15 | 0.6 | 64 | 2.6 |
| | 0.20 | 11.4 | 22 | 1.2 | 43 | 1.7 |
| | 0.40 | 16.6 | 24 | 2.4 | 38 | 1.5 |
| | 0.65 | 20.7 | 24 | 3.9 | 36 | 1.4 |
| Phenol | 0.01 | 4.0 | 10 | 0.06 | 100 | 3.6 |
| | 0.10 | 19.5 | 24 | 0.6 | 41 | 1.5 |
| | 0.20 | 27.5 | 34 | 1.2 | 28 | 1.0 |
| | 0.36 | 35.5 | 36 | 2.2 | 26 | 1.0 |

It can be seen that the number of solute molecules at the interface is increased about twentyfold by adsorption. (The figures in col. 5 were calculated by assuming that the interfacial zone was 10 Angstrom -

about two molecules ~ deep, whence the number of "molecules already present" = Volume of zone x Bulk concentration = $6 \times 10^{-13} C_W$).

Similar values to those in col. 6 were found by Harkins and coworkers, [36] p. 58. Area per molecule at $\Delta\sigma \approx 25$ were: Propionic acid 39, phenol 36.6. The interfacial value of 28 for phenol is significantly lower. It is possible that the phenyl group, being slightly polarized by its hydroxyl group, is attracted towards the water surface, so that the phenol molecule as a whole lies at an angle to the surface, resisting closer packing; whereas, at the interface this attraction is overcome by Van der Waals forces between the phenyl group and $CCl_4$.

The ratio in col. 7 is that of interfacial area per molecule (col. 6) to cross-sectional area of molecule (A). The latter quantity was estimated by the approximation:

$$A = \frac{\text{Molar Volume of Solute}}{N_A}^{\frac{2}{3}}$$

Combined Solutes. The data in table 3.4 are insufficient for accurate estimation, but the effect of the combined solutes seems to be a mutual decrease in $\Gamma$. Thus for a mixture of $C_{W,Pr} = 0.3$, $C_{W,Ph} = 0.2$, it was found that $\Gamma_{Pr} = 5 \times 10^{13}$, $\Gamma_{Ph} = 19 \times 10^{13}$, the

values of $\Gamma$ being thus $18 \times 10^{13}$ and $15 \times 10^{13}$ molecules less than for the individual solutes respectively.

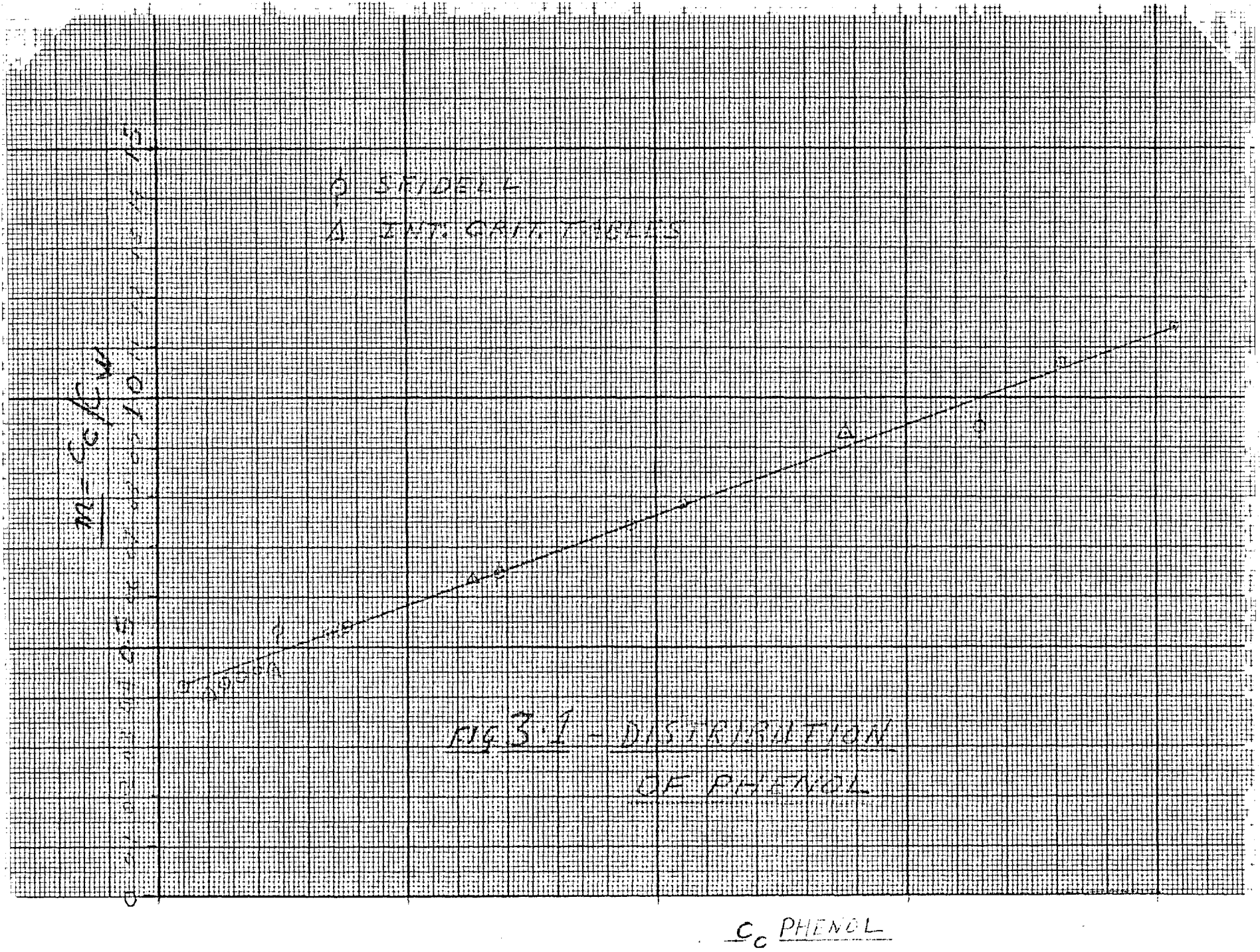



FIG 3.1 - DISTRIBUTION OF PHENOL

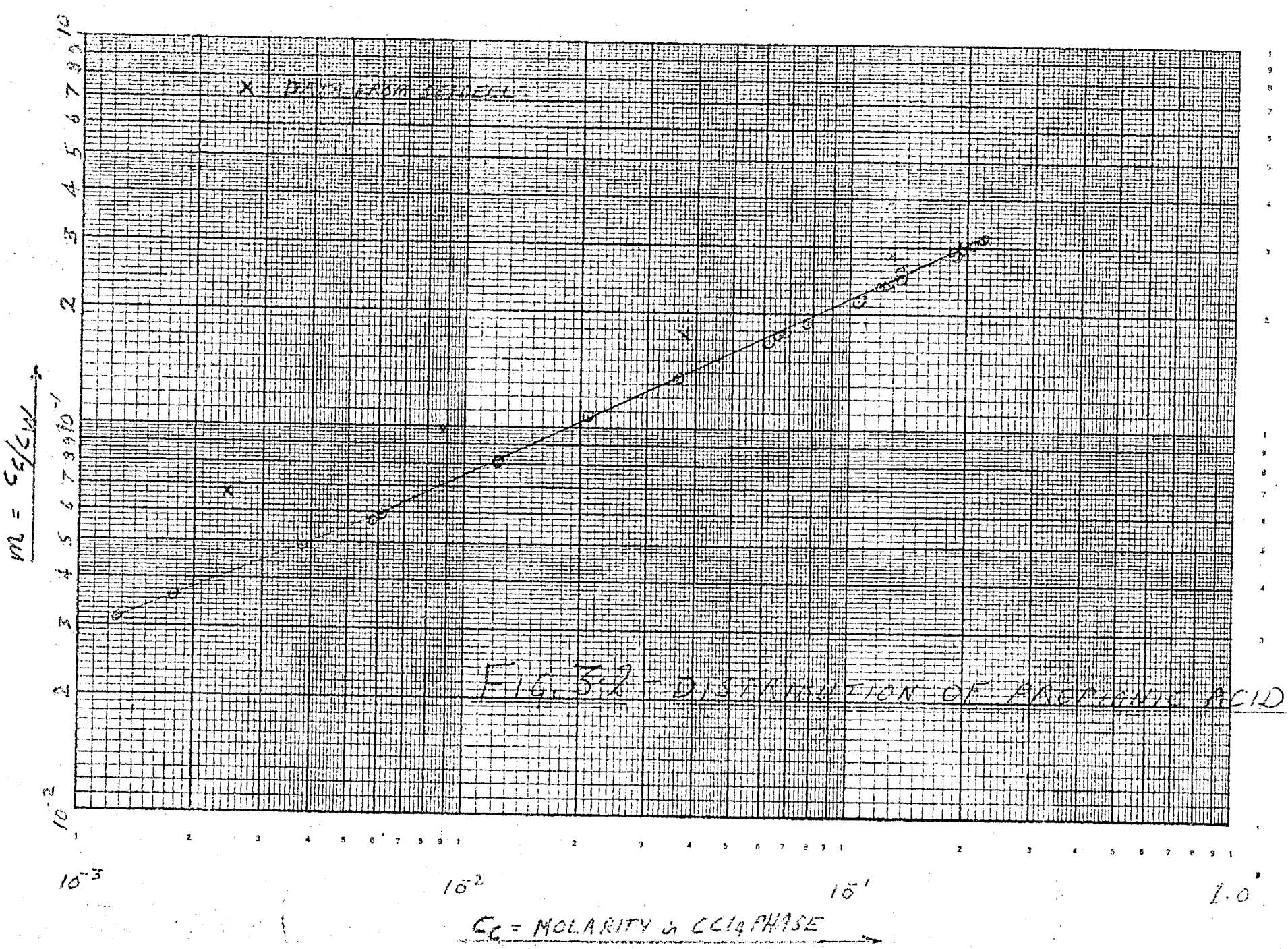



FIG. 52 - DISTRIBUTION OF PROPIONIC ACID

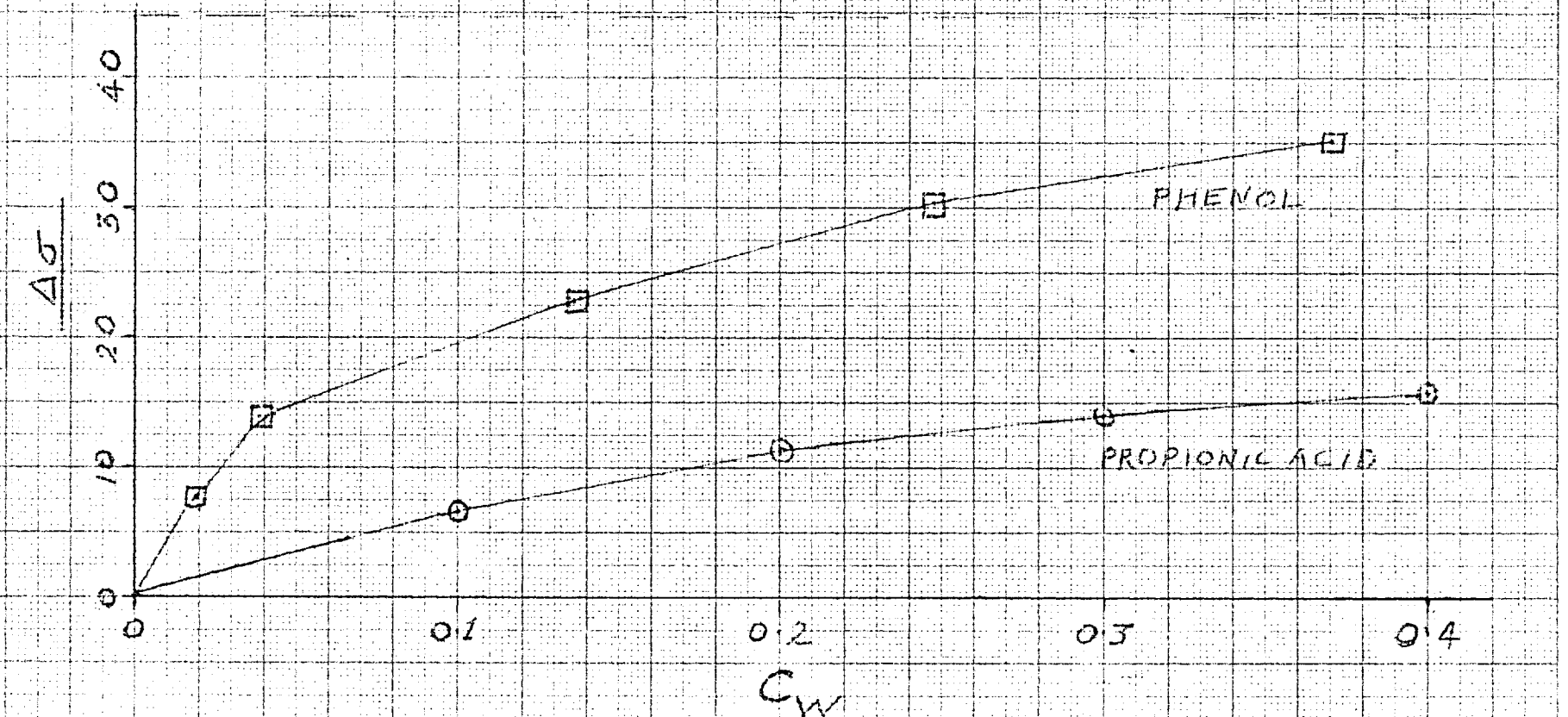



FIG. 3·3 - INTERFACIAL TENSION vs CONCENTRATION IN AQUEOUS PHASE

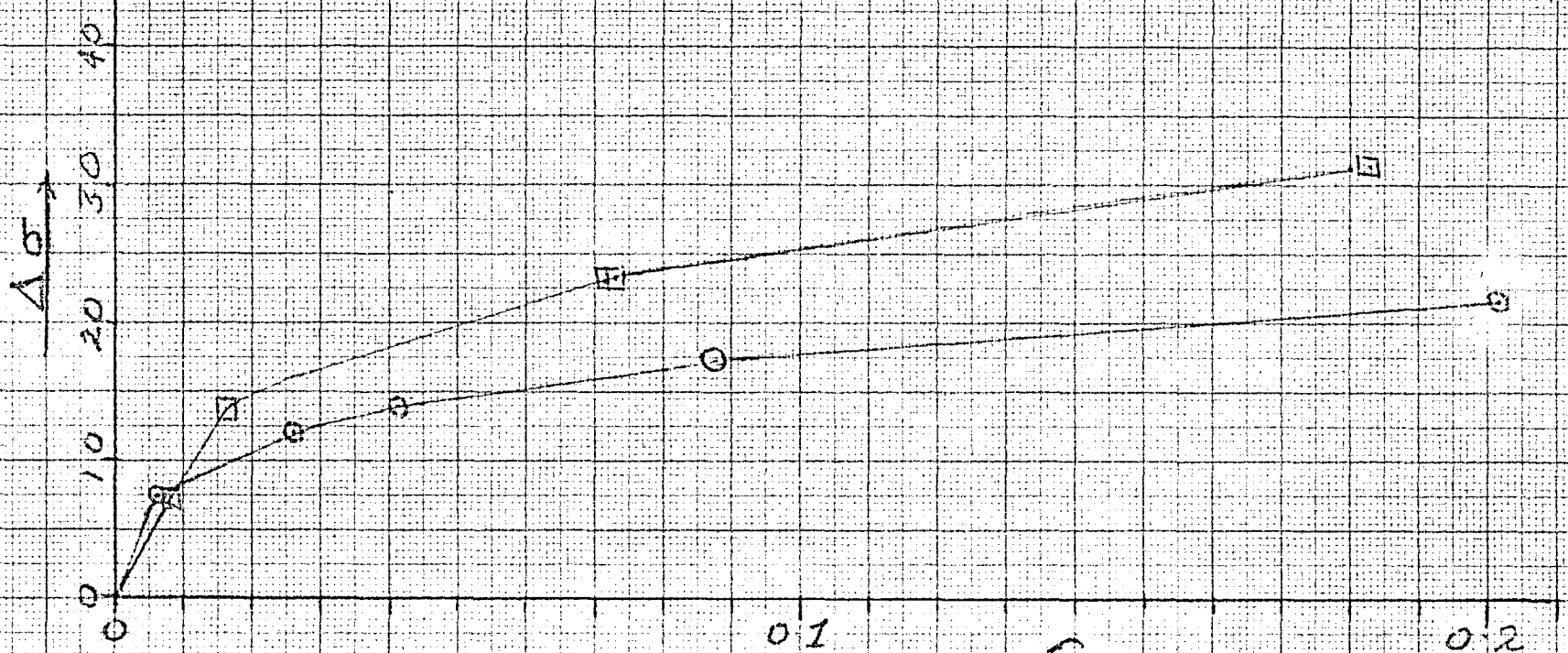



FIG 3·4 – INTERFACIAL TENSION VS CONCENTRATION IN $CCl_4$ PHASE

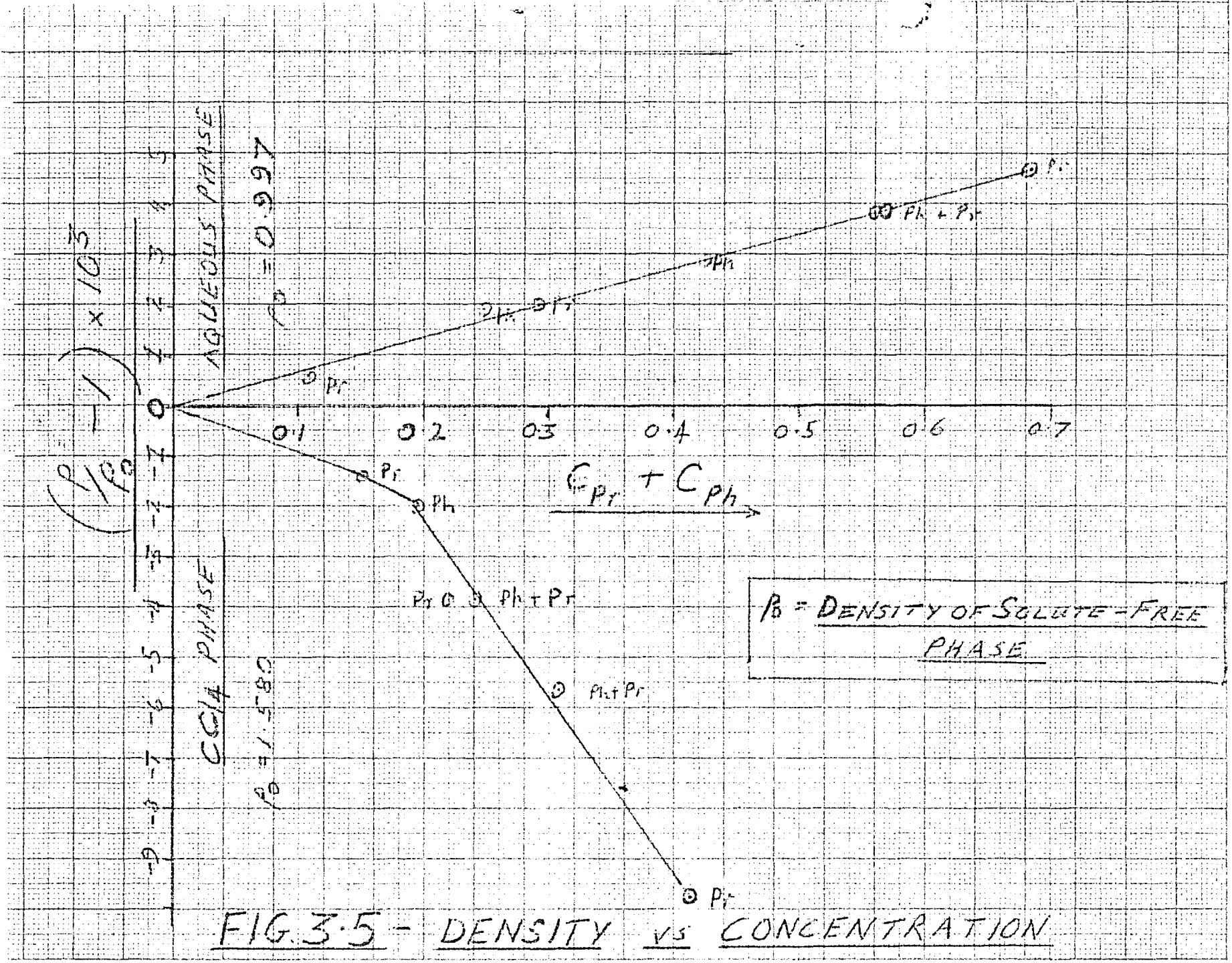



FIG. 3.5 - DENSITY VS CONCENTRATION

# CHAPTER FOUR

## Theoretical Considerations

### Mass Transfer

There are in the literature several different theoretical expressions for the overall mass transfer coefficient K, according to the different postulates for the mechanism of mass transfer between the two phases.

### 4.1. Penetration Theory

In the work of Bhattacharya [28], the equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (4\text{-}1)$$

is solved for diffusion of solute across the interface between two unstirred semi-infinite media A and B.

At any time $t^1$ the instantaneous individual mass transfer coefficients are

$$k'_A = \sqrt{\frac{D_A}{\pi t^1}}$$

$$k'_B = \sqrt{\frac{D_B}{\pi t^1}} \qquad (4\text{-}2)$$

and the instantaneous rate of mass transfer

$$N' = -D_A \left( \frac{\partial C_A}{\partial y_A} \right)_{y_A = o}$$

$$= -D_B \left( \frac{\partial C_B}{\partial y_B} \right)_{y_B = o} \qquad (4\text{-}3)$$

$$= k'_A \quad (C_{A,o} - C_{iA})$$

$$= k_B \quad (C_{iB} - C_{B,o}) \qquad (4\text{-}4)$$

where $C_{A,o}$ and $C_{B,o}$ are the bulk phase concentrations at $t' = o$, and the interfacial concentrations are in equilibrium so that

$$\frac{C_{iA}}{C_{iB}} = m_i \qquad (4\text{-}5)$$

From eqns. (4-2, 4-4, 4-5) it follows that the interfacial concentration is constant

$$C_{iA} = C_{iA,o} = m_i C_{iB,o}$$

$$= m_i \frac{C_{A,o}\sqrt{\frac{D_A}{D_B}} + C_{B,o}}{1 + m_i\sqrt{\frac{D_A}{D_B}}} \qquad (4\text{-}6)$$

The instantaneous overall mass transfer coefficient $K'_A$ can be defined from the above equations by using the principle of addition of resistances in series

$$\frac{1}{K'_A} = \frac{1}{k'_A} + \frac{m}{k'_B} \qquad (4\text{-}7)$$

$$N' = K'_A \quad (C_{A,o} - m_i C_{B,o}) \qquad (4\text{-}8)$$

$$K'_A = \sqrt{\frac{D_e}{\pi t'}} \qquad (4\text{-}9)$$

where $D_e$ will be called the overall effective diffusivity for phase A and is defined by

$$D_e = \frac{D_A}{1 + m_i \sqrt{\frac{D_A}{D_B}}} \qquad (4\text{-}10)$$

When applying the above equations to the results of chapter 5, it was necessary, since $m \propto C$, to obtain a solution of equation (4-6) by successive approximations. First a value of m was estimated and applied in equation (4-6) to obtain a first approximation $C_{ic,o}$, and hence, using the results of chapter 3, a second approximation m, which was applied in equation (4-6), etc. Usually three or four trials were sufficient.

By integration of equations (4-2, 4-9) with respect to $t'$, the total mass transferred across unit interfacial area up to time t

$$N = 2 \sqrt{\frac{Dt}{\pi}} \, \Delta C^{\ast} \qquad (4\text{-}11)$$

where D and $C^{\ast}$ refer to the corresponding quantities in any of equations (4-2, 4-9).

In the contact apparatus, the interface will move through a length Z at a velocity $u_i$, thus

$$t = Z/u_i \qquad (4\text{-}12)$$

For unit width of interface, the interfacial area produced per second is $u_i$. Each element of interface

remains in the apparatus for time $t = Z/u_i$. Thus in the apparatus as a whole, mass transferred per second

$$= \begin{pmatrix}\text{Mass transferred per}\\ \text{unit interfacial area}\end{pmatrix} \times \begin{pmatrix}\text{Interfacial area}\\ \text{produced per second}\end{pmatrix}$$

$$= NZ/t \qquad (4\text{-}13)$$

But, also, mass transferred in the apparatus per unit time

= (Flowrate) x (Change in Concentration)

$$= Q_A(C_{A,o} - C_{A,t}) = Q_A \Delta C_A \qquad (4\text{-}14)$$

From (4-11, 4-13, 4-14)

$$\frac{Q\Delta C}{Z\Delta C^*} = \frac{QE}{Z} = 2\sqrt{\frac{D}{\pi t}} \qquad (4\text{-}15)$$

where E is called the fractional extraction.

In particular

$$K_R = \frac{Q_A(C_{A,o} - C_{A,t})}{Z(C_{A,o} - m_i C_{B,o})}$$

$$= \frac{Q_A E}{Z} = 2\sqrt{\frac{D_e}{\pi t}} \qquad (4\text{-}16)$$

where the time average overall mass transfer coefficient for initial concentration driving force based on phase A has been given the subscript R because it is used as a standard of reference in the subsequent sections.

The significance of the above equations is that, since the interfacial concentration is constant under the

conditions for which they are valid - namely, shallow penetration - one can apply to diffusion of a solute between two liquid phases the equations developed in the literature for penetration into a liquid from a pure gas, with constant interfacial concentration (§§4-3, 4-4, 4-5).

## 4.2 Penetration from Pure Gas into Viscous Film

PIGFORD [40] solved the diffusion equation (4-1) for the case of a pure gas and a liquid film of thickness B, in viscous motion, with parabolic velocity profile having a maximum at the interface.

Expressed in terms of the fractional extraction $E = \Delta C/\Delta C^{*}$

$$E_A = \frac{C_{A,o} - C_{A,t}}{C_{A,o} - C_{iA}}$$

$$= 1 - 0.787 \exp(-5.121\beta) - 0.1001 \exp(-39.31\beta) - 0.036 \exp(-105.6\beta) - 0.0181 \exp(-204.7\beta) \qquad (4\text{-}17)$$

where $\beta = D_A t/B^2$ (4-18)

For short contact times (i.e. low $\beta$)

$$\frac{C_{A,o} - C_{A,t}}{C_{A,o} - C_{iA}} = 3\sqrt{\frac{Dt}{\pi B^2}} \qquad (4\text{-}19)$$

i.e. $E_A = 3\sqrt{\beta/\pi}$ (4-19a)

For parabolic velocity profile,

$$Q_A = \frac{2}{3} u_i B = \frac{2Bz}{3t}$$

whence, on multiplying both sides of equation (4-19) by $Q_A$, one obtains the semi-infinite unstirred medium equation (4-15)

$$k_A = \frac{Q_A E_A}{Z} = 2\sqrt{\frac{D_A}{\pi t}}$$

A simple method of seeing whether p is low enough to use equation (4-15) instead of equation (4-17) is to plot the % error x vs p , where from equations (4-17, 4.19)

$$\varkappa = \frac{E(4\text{-}17) - E(4\text{-}19)}{E(4\text{-}17)} \times 100$$

In the range $0.1 < p < 0.2$, the error is $1 < x < 5\%$, corresponding, for b = 0.01 and $D = 10^{-5}$, to $0.55 < E < 0.75$.

For a laminar vertical liquid film the criterion of short contact time given by DANCKWERTS [41] is

$$\frac{zD_A\mu_A}{g\rho_A B^4} < 0.1 \qquad (4\text{-}20)$$

for 5% accuracy.

Since, from § 2.9 ,

$$B^3 = 3\mu Q/g\rho \text{ and } z/t = 1.5\ Q/B$$

equation 4-20 reduces to $p < 0.2$.

In equation (4-17), for long contact times all terms except the first can be neglected and the mass transfer coefficient - based now on the log mean driving force - tends to a constant

$$k_{A,l.m} = \frac{Q_A}{Z} \ln E_A = 3.41 \frac{D_A}{B} \qquad (4\text{-}21)$$

## 4.3 Random Surface Renewal.

Under turbulent conditions, fresh liquid from the interior is likely to displace liquid at the interface. The theory of DANCKWERTS [41] assumes that surface is randomly replaced at a fractional rate s (area per unit area) per unit time. Let $\psi(t')dt'$ be the fraction of unit area occupied by surface of age $t' < (t' + dt')$. Then the fraction which does not survive to age $(t' + dt')$ $= - d\psi(t')$

$$- d\psi(t') = \psi(t') . s . dt \qquad (4\text{-}22)$$

$$\therefore \quad \psi(t') = Ae^{-st'} \qquad (4\text{-}23)$$

Since the sum of the fractional areas of all ages is unity,

$$\int_0^\infty \psi(t')\, dt' = 1 \qquad (4\text{-}24)$$

$$\therefore \quad \psi(t') = se^{-st'} \qquad (4\text{-}25)$$

Let mass transfer into phase A be governed by the rate of diffusion into element of area $\psi(t')dt$, and let the concentration driving force $\Delta C_A^*$ be constant. From (4-2), (4-25), the rate of mass transfer into element of age $t'$ is

$$N(t') = se^{-st'} \sqrt{\frac{D_A}{\pi t'}}\, dt'$$

whence, summing for all ages, $0 < t' < \infty$ ,

$$k_A = \sqrt{D_A s} \qquad (4\text{-}26)$$

4.3a Short Contact Time.

In the moving film contactors, such as a wetted wall column, the upper age limit cannot exceed the contact time t i.e. $0 < t' < t$. Consider unit area of interface, 1, at time t; it will be composed of elementary areas of age $t'$

$$a(t') = \psi(t')\, dt' \qquad (4\text{-}27)$$

Since $\psi$ is here a function both of t and $t'$, equation (4-22) becomes

$$d\psi = \frac{\partial \psi}{\partial t}\, dt + \frac{\partial \psi}{\partial t'}\, dt'$$

$$= -s\psi dt = -s\psi dt' \qquad (4\text{-}28)$$

whence it follows that $\psi$ is made up of two parts:

$$a(t') = a(t'=o)e^{-st'}$$

and $$a(t) = a(t=o)e^{-st} \qquad (4\text{-}29)$$

where $a(t' = o)$ is the initial area occupied by surface elements of age $t'$.

It follows from the definition of s that the amount of fresh surface entering the unit area, 1, in time dt is sdt; let it enter at time

$$t'' = t - t' \qquad (4\text{-}29)$$

$$a(t'') = sdt \qquad (4\text{-}30)$$

But, from (4-29) and the definition of t, the necessary and sufficient condition for an element to be of an age $t'$ at contact time t is that it should have

entered the area 1 at time $t''$,

i.e. $t''$ is the origin of $t'$

From (4-29,-30)

$$a(t'') = a(t' = o)$$

i.e. $$a(t' = o) = sdt \qquad (4\text{-}31)$$

From (4-28, - 29)

$$a(t') = se^{-st'}\,dt' \qquad (4\text{-}32)$$

which, from (4-27), is equivalent to (4-25).

Consider now those elements of age t, which entered at t = o.

From (4-27)

$$a(t) = a(t = o)\, e^{-st} \qquad (4\text{-}27a)$$

But $a(t = o)$ differs from $a(t' = o)$, $0 < t' < t$ in that the elements of age t did not enter by the random surface renewal mechanism - at a rate s, in amounts sdt - but were introduced at time t = o in the form of an impulse function of size 1,

i.e. $$a(t = o) = 1 \qquad (4\text{-}31a)$$

$$a(t) = 1 \cdot e^{-st} \qquad (4\text{-}32a)$$

<u>Check</u>: (i) The sum of all elementary areas should equal 1.

From (4-32, - 32a)

$$e^{-st} + s\int_o^t e^{-st'}\,dt' = 1$$

(ii) As $st \to 0$, the total fraction of surface which has been renewed,

$$\sum a(t') = \int_0^t \psi(t')dt \to st.$$

Equation (4-32a) obeys this condition:

$$t \to o, \quad a(t) = e^{-st} \to 1 - st$$

$$1 - a(t) \to st$$

$$\sum (a(t') = s\int_0^t e^{-st'} dt' \to st$$

(iii) As $st \to o$, very few areas have been renewed more than once, so that

$$a(t') \to sdt$$

Equation (4-32) obeys the above condition.

Rate of mass transfer into unit area at time t.

Assume, as for (4-26), that $\Delta C^*$ is constant, hence

$$\frac{N(t)}{\Delta C^*} = \int_0^t \psi(t') \sqrt{\frac{D}{\pi t'}}\, dt' \qquad (4\text{-}33)$$

From (4-32, - 32a, -33)

$$\frac{N(t)}{\Delta C^*} = e^{-st}\sqrt{\frac{D}{\pi t}} + \int_0^t se^{-st'}\sqrt{\frac{D}{\pi t'}}\, dt'$$

$$\frac{N(t)}{\Delta C^*} = e^{-st}\sqrt{\frac{D}{\pi t}} + \sqrt{Ds}\ \operatorname{erf}\sqrt{st} \qquad (4\text{-}34)$$

where $\operatorname{erf}\sqrt{st} = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{st}} e^{-st'}\, d\sqrt{st'}$

Total amount of mass transferred across unit area

up to time t is given by

$$\int_o^t N(t)\,dt \qquad (4\text{-}35)$$

From (4-34, - 35)

$$\frac{1}{\Delta C^{*}} \int_o^t N(t)\,dt = \sqrt{\frac{D}{s}}\ \operatorname{erf}\sqrt{st} + \sqrt{Ds}\int_o^t \operatorname{erf}\sqrt{st}\,dt \qquad (4\text{-}36)$$

Time average mass transfer coefficient:

$$k = \frac{1}{\Delta C^{*} t}\int_o^t N(t)dt \qquad (4\text{-}37)$$

From (4-36,-37)

$$k = 2\sqrt{\frac{D}{\pi t}}\left(\sqrt{\frac{\pi}{4st}}\ \operatorname{erf}\sqrt{st} + \sqrt{\frac{\pi s}{4t}}\int_o^t \operatorname{erf}\sqrt{st}\ dt\right)$$

$$= 2\sqrt{\frac{D}{\pi t}} \cdot F \qquad (4\text{-}38)$$

where

$$F = \sqrt{\frac{\pi}{4st}}\left((st + \tfrac{1}{2})\operatorname{erf} st + e^{-st}\sqrt{\frac{st}{\pi}}\right)$$

Check:

(i) $st \to o$

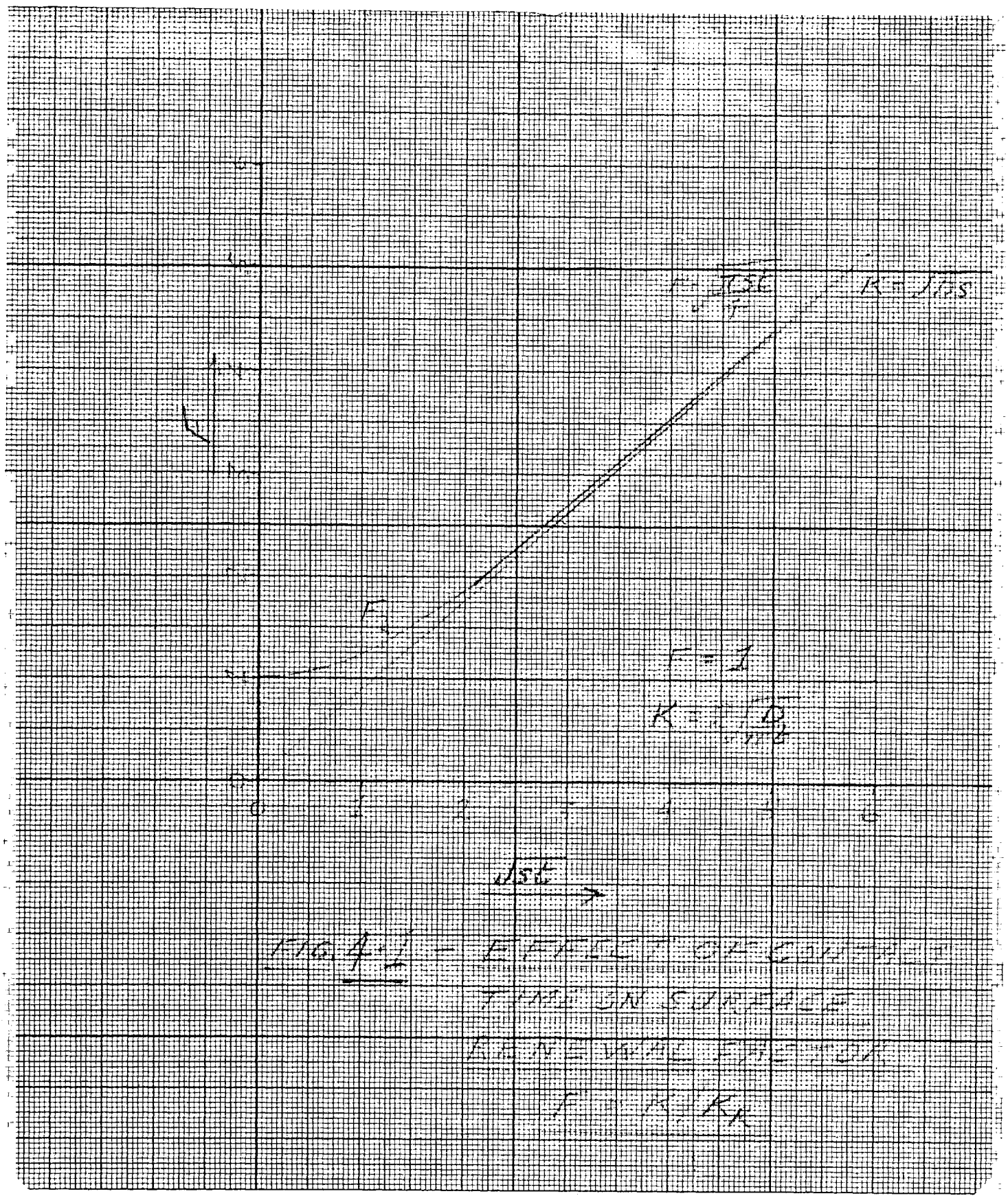
$F \to 1$

$k - 2\sqrt{\frac{D}{t}}$ i.e. Equ. (4-15)

(ii) $st \to oo$

$F \to \sqrt{\frac{\pi st}{4}}$

$k \to Ds$ i.e. Equ. (4-26).



Numerical Values: Since s and t always appear together as product, F should be a function of st. Hence a graph is plotted of F vs $\sqrt{st}$, (Fig. 4.1).

Log. Mean Driving Force: Consider an element of film at contact time $t = Z/u_i$. A mass balance gives

$$-Q_B\, dC_B = Q_A dC_A = -\, k(t)\Delta C_A^{*}\, dz \qquad (4\text{-}39)$$

From equations (4-7,-39) it can be shown that

$$(1 + mQ_B/Q_A)\; dC_A = d(C_A - mC_B) \qquad (4\text{-}40)$$

whence equation (4-39) can be written

$$\frac{Q_A d(C_A - mC_B)}{1 + mQ_B/Q_A} = -\, K(t)(C_A - mC_B)u_i\, dt \qquad (4\text{-}41)$$

whence the log. mean driving force follows

$$\text{i.e.}\quad \frac{Q_A(C_{A,o} - C_{A,t})}{Z(C_A - mC_B)_{lm}} = \frac{1}{t}\int_o^t K(t)dt \qquad (4\text{-}42)$$

By substituting from equations (4-7 to -15) for the L.H.S, and from equation (4-38) for the R.H.S., equation (4-42) may be written

$$\frac{Q\Delta C}{Z\Delta C^{*}_{l.m.}} = 2\sqrt{\frac{D}{\pi t}}\;.F$$

$$\text{i.e. } k_{l.m.} = k_R\,.F \qquad (4\text{-}43)$$

4.4. TOOR and MARCHELLO [42] developed the "film-penetration" model of surface renewal theory, which postulates a finite distance L over which the concentration changes from "well mixed bulk" value $C_A$ to interfacial value $C_{iA}$. The significance of this model is that

whereas transfer into the younger elements of the surface approximates to the "semi-inf. unstirred" equations (4-15), transfer through the older elements approximates to the steady state equation $k = D/L$. The criterion of short life is $s \gg D/L^2$, and for $s \gg\gg D/L^2$ the equations of TOOR and MARCHELLO reduce to those of DANCKWERTS. In the vertical film, § 2, $L = B = 10^{-2}$, so that for $s \gg\gg 10^{-1}$ the equations of § 4·3 are close enough.

## 4.5 Eddy Diffusivity

Under certain conditions the diffusivity D may be replaced by a combined molecular and eddy diffusivity (D + e). Thus

$$\frac{\bar{C}}{t} + \nabla (\overline{UC}) = (D + e) \nabla^2 \bar{C} \qquad (4\text{-}44)$$

This equation holds strictly only for isotropic, homogeneous turbulence, and implies a simplified theory of eddy transfer which neglects transfer from the eddy during its motion between two points. Moreover, the assumption of constant eddy diffusivity e holds only for diffusion distances greater than the scale of turbulence.

These conditions would seem to preclude the use of this theory on the results of chapter 5; firstly because in the case of waves and ripples on the interface, the turbulence is not uniform, secondly because in the case

of "eruptions" the turbulence is not uniform and its scale is apparently of the order of the diffusion distance. These points will be referred to later, in discussion of the results.

4.6 Boundary Layer Theory.

The model where the bulk of the liquid is turbulent, but where turbulence dies away near the interface - the "laminar boundary layer" theory [43] does not cover the present case, where flow is laminar except for the interface which can generate turbulence. However, it is doubtful how far this theory can apply to a liquid-liquid interface. The basic assumption is that eddies die away near the interface, which in turn implies that the interface acts as a rigid surface; whereas many observations of such phenomena as drop recirculation and coalescence (of Linton and Sutherland [5]), and of interfacial eruptions e.g. plate 5.7 show that motion in the liquid near the interface takes place fairly readily.

The laminar boundary layer theory and the surface renewal theory for high s are opposite extremes, and at present it is not certain under what conditions each is valid in liquid - liquid systems. The results of SHERWOOD and GORDON, [6], § 1.6, are in accord with the

surface renewal theory in that $K = A\sqrt{D_e}$. Examination of the results of LEWIS, [2], § 1.3, show that for each system k varies almost linearly with the sum of the stirrer speeds, whereas from boundary layer theory one would expect variation of K with the square root of their relative velocity.

## 4.7 Dynamic Interfacial Tension.

When two liquids containing a surface active solute are freshly contacted, the interfacial tension varies with time because the interfacial excess of solute, $\Gamma$, predicted by the Gibbs adsorption isotherm (§ 3.18) is not present in a fresh interface and needs time to build up. As $\Gamma$ increases, $\sigma$ decreases, hence $\Delta\sigma$, the surface pressure, increases. For low concentrations the relationship is that of a two-dimensional ideal gas

$$\Delta\sigma = RT\Gamma \qquad (4\text{-}45)$$

The initial value of interfacial tension is near that for the solute-free liquids; the final value is that in equilibrium with concentration $C_{iA}$ just below the interfacial zone. The variation of $\Gamma$ and hence of $\sigma$ with time is solved below, for the case of mass transfer across the interface by diffusion alone. The assumptions follow those of RIDEAL and SUTHERLAND [44] for the air-water surface.

If $\Gamma$ is the amount adsorbed at a concentration $C_B$, we define an interfacial concentration distribution coefficient

$$M = \Gamma / C_B \qquad (4\text{-}46)$$

An average value of M is

$$M = \frac{\int_o^{C_B} \left(\Gamma / C_B\right) dC_B}{\int_o^{C_B} dC_B} \qquad (4\text{-}47)$$

From the Gibbs equation (3-7) in (4-47)

$$M = \Delta\sigma / RTC_B \qquad (4\text{-}48)$$

The diffusion equation, neglecting diffusion in the plane of the interface is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2} \qquad (4\text{-}1)$$

Boundary Conditions:

(i) $y = o$, $t > o$, at interface

Input - Output = Accumulation

$$D_A \frac{\partial C_A}{\partial y_A} + D_B \frac{\partial C_B}{\partial y_B} = M \frac{\partial C_{iB}}{\partial t} \qquad (4\text{-}49)$$

(It is of interest to note that SCRIVEN and STERNLING [9], § 1.8, in setting the R.H.S of equation (4-49) equal to zero, would appear to be neglecting the dynamic interfacial tension of an interface which is being renewed without change of area.)

(ii) No resistance at the interface; the adsorbed

layer is simultaneously in equilibrium with the solute in both phases: hence these are in equilibrium with each other. (The electrical analogy would be two wires joined to each other through the centre of a large, thin copper disc).

$$C_{iA} = mC_{iB}$$

(iii) $t = o, \quad y_A > o, \quad C_A = C_{A,o}$

(iv) $t = o, \quad y_B > o, \quad C_B = C_{B,o}$

(v) No initial interfacial excess,

$$t = o, \quad y = o, \quad \Gamma_o = 0$$

(vi) Interfacial concentration finally approaches the "semi infinite unstirred" value, equation (4-15)

$$y = o, \; t \to \infty, \quad C_{iB\infty} = \frac{C_{Ao}\sqrt{D_A} + C_{B,o}\sqrt{D_B}}{m\sqrt{D_A} + \sqrt{D_B}}$$

also, $$\Gamma_\infty = MC_{iB\infty}$$

The above equations were solved by the Laplace transform method, to yield

$$\frac{\Delta\sigma_t}{\Delta\sigma_\infty} = \frac{\Gamma_t}{\Gamma_\infty} = \frac{C_{iB,t}}{C_{iB,\infty}} = 1 - e^{a^2 t}\,\operatorname{erfc}\, a\sqrt{t} \qquad (4\text{-}50)$$

where

$$a = \frac{m\sqrt{D_A} + \sqrt{D_B}}{M} \qquad (4\text{-}51)$$

and has the dimensions $T^{-\frac{1}{2}}$

## Numerical Values

$$M = \Delta\sigma / C_B RT$$

where $C_B$ is in mol/cc

and $R = 8.3 \times 10^7$ ergs $^{o}C^{-1}$ $mol^{-1}$

Propionic Acid: Let $C_B = 0.12/1000$

$m = 0.1$

$\Delta\sigma = 7.5$

$M = 2.5 \times 10^{-6}$ cm

$a = 1.5 \times 10^3$

Phenol: $C_B = 0.12/1000$, $m = 0.5$, $\Delta\sigma = 21$

$M = 7.2 \times 10^{-6}$ cm

$a = 0.71 \times 10^3$

Table 4.1: $\Gamma_t / \Gamma_\infty$

| t secs | $10^{-7}$ | $10^{-6}$ | $10^{-5}$ | $10^{-4}$ |
|---|---|---|---|---|
| Propionic Acid | 0.37 | 0.68 | 0.88 | 0.97 |
| Phenol | 0.21 | 0.48 | 0.76 | 0.91 |

From table 4.1 it appears that diffusion is adequate to supply the interfacial excess at normal rates of expansion, which would be of the order of 10 cm per sec [44]. Suppose some small area A of interface becomes the seat of contact of richer liquid - vid. § 5.9(iii) - then, from tables 4.1, 4.2, this element has to wait about $10^{-4}$ sec before its inter-

facial pressure is high enough for it to expand. Assuming that it expands radially to form a disc, and that the central area of the disc will once again contain fresh liquid sucked in from the interior by the outward motion of the interface, then this new area will also have to wait $10^{-4}$ secs before it can expand and be replaced in turn, so that the original small area A can, on this basis, be renewed about $10^{4}$ times per second.

Looked at from the point of view of surface pressure, the results of tables 4.1, 4.2, show that phenol is about ten times slower than propionic acid to produce a positive interfacial pressure. Table 4.2 shows the difference in interfacial pressures, between $\Delta\sigma_t$ of the outward moving disc and $\Delta\sigma_R$ of the undisturbed interface, taking the values of Table 5.14, § 5.9(iii), for the contact of water and 0.2 M $CCl_4$ solutions of phenol and propionic acid respectively.

Table 4.2: $\Delta\sigma_t - \Delta\sigma_R$

| t | $10^{-7}$ | $10^{-6}$ | $10^{-5}$ | $10^{-4}$ | |
|---|---|---|---|---|---|
| Ph. | -14 | -7 | +0.5 | +4 | +7 |
| Pr | -6 | -0.5 | +3 | +5 | +5 |

It is seen that although the older elements have a positive pressure with respect to their surroundings, and

hence must continue to expand, the younger elements are in a state of compression, especially in the case of phenol. Thus it is likely that although, once richer liquid has contacted an area of the interface, diffusion is soon adequate to allow the expansion of that area at a rate which would seem to be limited mainly by interfacial pressure and viscosity, there exists initially a force resisting the outward motion of the interface with its concomitant motion of liquid from the interior up to the interface.

# CHAPTER FIVE

## Results and Discussion

Results are presented in §§ 5.3 - 5.8, and the main findings are reviewed in § 5.9.

5.1 Nomenclature: (a) Concentration

The runs will be designated by their initial concentrations, written in the following order:

$$C_{C,Pr},\ C_{C,Ph}\ /\ C_{W,Pr},\ C_{W,Ph}$$

Thus 0.2, 0/0, 0.05

stands for initial concentrations of 0.2 Molar propionic acid in the $CCl_4$ phase, and 0.05 M phenol in the water phase.

(b) Mass Transfer Coefficients are reported in several ways, in accordance with the preceding theoretical sections (Chapter 4), with driving force $\triangle C^{x} = (C_C - mC_W)$ based on the $CCl_4$ phase, and distribution coefficient $m = C_{iC}/C_{iW}$ calculated according to equation (4-6) at the interfacial concentration

$$C_{iC} = m\,\frac{C_C\sqrt{D_C/D_W} + C_W}{1 + m\sqrt{D_C/D_W}} \qquad (5\text{-}1)$$

(i) From equations (4-7,-9,-10) the reference coefficient

$$K_R = \sqrt{\frac{D_e}{\pi t}} \qquad (5\text{-}2)$$

where t is the contact time, $t = Z/U_i$, and the effective diffusivity $D_e$ is defined by

$$\sqrt{D_e} = \frac{\sqrt{D_C}}{1 + m\sqrt{D_C/D_W}} \qquad (5\text{-}3)$$

(ii) The coefficient based on the initial driving force, from equation (4-16)

$$K_{In} = \frac{Q_C(C_{C,o} - C_{C,t})}{Z(C_{C,o} - mC_{W,o})}$$

$$= Q_C \Delta C_C / Z \Delta C_C^{\ast} = Q_C E/Z \qquad (5\text{-}5)$$

For absorption into a semi-infinite stagnant medium, with no interfacial resistance

$$K_{In} = K_R \qquad (5\text{-}6)$$

(iii) Log. mean coefficient, $K_{lm}$.

$$K_{lm} = \frac{Q_C(C_{C,o} - C_{C,t})}{Z(C_C - mC_B)_{lm}} \qquad (5\text{-}4)$$

If the theory of § 4·3a is valid,

$$K_{lm} = K_R F(s,t) \qquad (5\text{-}7)$$

In both the two cases, (i) and (ii) above, transfer of two solutes under identical driving forces takes place in the ratio of the square root of their effective diffusivities;

$$K_{Pr}/K_{Ph} = \sqrt{D_{e,Pr}/D_{e,Ph}} \qquad (5\text{-}8)$$

(c) Statistical Terms [45]

X % Deviation: $$X = \left( \frac{\text{calc.} - \text{obs.}}{\text{calc.}} \right) Y \times 100 \qquad (5\text{-}9)$$

Mean Deviation: $$\bar{x} = \frac{1}{n}\sum_{r=1}^{n} x_r \qquad (5\text{-}10)$$

Standard Error: $$\sigma = \sqrt{\frac{\sum_{r=1}^{n} (x_r - \bar{x})^2}{n(n-1)}} \qquad (5\text{-}11)$$

(1-2P)% Confidence Limits, $\bar{X} = \bar{x} \pm b$: Signified "confidence" that only P% of all future mean deviations $\bar{X}$ will differ from the present $\bar{x}$ by more than the "limits" b either way.

t-test, P: where $$t = \frac{\bar{x}_R - \bar{x}}{\sigma} \qquad (5\text{-}12)$$

Signifies that the odds are (1-P) to P against a given experimental result being merely due to a chance accumulation of random errors. When P = 5% the result is usually referred to as "significant", and when P = 1% as "highly significant" of the presence of some consistent factor.

## 5·2 Tabulation

Table 5·1 is a list of the experimental results which are tabulated in Appendix (2).

Table 5·1: List of Results (see Appendix 2)

(i) Vertical Contactor

| Runs No. | Initial Concentrations | Number of Observations | Range of Contact Times | Range of Fractional Extraction | |
|---|---|---|---|---|---|
| | | | | $E_{Pr}$ | $E_{Ph}$ |
| 1 | 0.2,0/0,0 | 7 | 1.0-5.8 | 0.79-0.97 | |
| 2 | 0.1,0/0,0 | 5 | 1.0-3.4 | " | |
| 3 | 0.05,0/0,0 | 5 | " | " | |
| 4 | 0,0.05/0,0 | 11 | 0.42-7.1 | | 0.41-0.89 |
| 5 | 0,012/0,0 | 9 | 1.0-7.1 | | " |
| 6 | 0,0.22/0,0 | 9 | " | | " |
| 7 | 0.2,0.05/0,0 | 12 | 0.42-7.1 | 0.65-0.97 | 0.45-0.90 |
| 8 | 0.12,0.12/0,0 | 6 | 1.0-3.4 | " | " |
| 9 | 0.05,0.22/0,0 | 9 | 1.0-7.1 | " | " |
| 10 | 0.2,0.2/0,0 | 3 | 1.0-1.6 | 0.7 | 0.5 |
| 11 | 0.2,0/0,0.05 | 8 | 0.49-6.0 | 0.55-0.98 | 0.40-0.95 |
| 12 | 0,0.05/0.5,0 | 12 | 0.49-9.0 | 0.3-0.9 | 0.3-0.8 |
| 13 | 0,0/0.8,0.2 | 2 | 2.86,8.82 | 0.1 | 0.1 |
| 14 | 0,0/0.05,0.05 | 3 | 2.86,13.8 | " | " |
| 15 | 0,0/0.8,0 | 2 | 2.86,8.82 | " | " |
| 16 | 0,0/0.05,0 | 2 | " | " | " |
| 17 | 0,0/0,0.05 | 2 | 2.86,13.8 | " | " |
| 18 | 0,0/0,0.2 | 2 | 2.86,8.82 | " | " |

(ii) Horizontal Contactor

| Runs No. | Initial Concentrations | Number of Observations | Range of Contact Times | Fractional Extraction $E_{Pr}$ | $E_{Ph}$ |
|---|---|---|---|---|---|
| 19 | 0.2,0.05/0,0 | 5 | 225-775 | .35-.95 | .25-.67 |
| 20 | 0.2,0/0,0.05 | 1 | 181 | " | " |
| 21 | 0.1,0/0,0.05 | 4 | 273-900 | " | " |
| 22 | 0,0.2/0,0 | 5 | 187-473 | " | " |
| 23 | 0,0.1/0,0 | 1 | 206 | " | " |
| 24 | 0,0.05/0,0 | 2 | 338 | " | " |
| 25 | 0,0.05/0.5,0 | 1 | 495 | " | " |
| | (iii) Vertical Contactor - Surface Active Agent | | | | |
| 26 | 0.1,0.1/0,0 | 5 | 1.25-3.6 | 0.1 | 0.1 |
| 27 | 0.2,0/0,0.2 | 2 | 1.78, 2.32 | " | " |
| 28 | 0,0/0.6,0.3 | 3 | 2.42-3.6 | 0.2 | 0.3 |
| 29 | 0,0.1/0.6,0 | 2 | 2.42,3.6 | 0.2 | 0.2 |
| 30 | 0,0.2/0.3,0 | 1 | 9.0 | 0.2 | 0.3 |

## 5.3 Transfer of Solutes from $CCl_4$ to Water (Direction C → W) Runs 1-10

These runs were performed with $CCl_4$ as the film phase (v. § 2.5), at Film Reynolds numbers Re of 4.6, 8.0 and 14.7. Column heights, Z, were 2.2, 5.2, 11.2 and 23 cm.

For each value of Re, $K_{1m}$ was plotted against Z on log-log paper (Fig 5.0). It was found that especially for the longer contact times $K_{1m}$ decreased with time:

$$K_{1m} \propto t^{-n} \qquad 0.5 < n < 1.0 \qquad (5\text{-}13)$$

The exponent of t is unexpectedly large, since on the one hand the equations of Bhattacharya (5-2) predict $K = At^{-0.5}$, while, at the other extreme, the surface renewal theory of Danckwerts (XXX) predicts $K = At^{0}$. Neither the modified surface renewal equations (§ 4.3a) nor the streamline - penetration equations of Emmert and Pigford (4.2) were sufficient to account for the high rate of decrease of K. Thus another explanation was sought.

On attempting to time the interface by injecting water-soluble dye in the water phase, an eruptive disturbance was noticed in the dyed streamlines at the top of the column. The presence of spontaneous interfacial "eruptions" was later confirmed by schlieren observation with the horizontal contactor (Plates 5).

Hence it was postulated firstly that these "eruptions produce an initial enhancement of K because of surface renewal, secondly that the rate of surface renewal decreases with time, with an exponent near $t^{-1}$, for reasons discussed in § 5.9(i) and (iii).

An attempt was made to separate the initial high extraction rate as an entry effect. Thus plots of fractional extraction E vs Z show an approximately linear relation after Z = 5.2 cm (Figs 5.1, 5.2). Assuming that the equations (5-1 to 6) - i.e. those for an undisturbed semi-infinite medium - applied to the latter section, then

$$\frac{Qc}{Z} \cdot \frac{(C_{c,o} - C_{c,t})}{(C_{c,o} - mC_{W,o})} = 2\sqrt{\frac{De}{\pi t}} \qquad (5\text{-}6)$$

But $Z = U_i t$

hence $$\frac{dE}{d\sqrt{Z}} = \sqrt{\frac{U_i}{Q_c}} \cdot 2\sqrt{\frac{D_e}{\pi}} \qquad (5\text{-}18)$$

However, by the time interfacial eruptions have ceased - say at $Z_1$ - the interfacial concentration has changed because of surface renewal to $C_{iZ_1}$, given by equation (5-1).

Hence $$\frac{dE}{d\sqrt{Z}} = 2\sqrt{\frac{D_e}{\pi} \cdot \frac{U_i}{Q_c}\lambda} \cdot \frac{(C_{c,Z_1} - mC_{W,Z_1})}{(C_{c,o} - mC_{W,o})} \qquad (5\text{-}19)$$

Table 5.2 gives the comparison between actual and predicted values of $dE/d\sqrt{Z}$.

Table 5.2: × % Deviation, $\partial E/\partial\sqrt{Z}$

| Re | Fig. 5.1: Simultaneous Transfer | | Fig. 5.2: Separate Transfer | |
|---|---|---|---|---|
| | Acid | Phenol | Acid | Phenol |
| 4.6 | +45 | -40 | +29 | +13 |
| 8.0 | | | -3 | -4 |
| 14.7 | -35 | +21 | 0 | -40 |

Mean Deviation $\bar{x}$ = -1.4

Std. Error $\sigma$ = 9.4

95% Confidence Limits = ±21%

The agreement is as close as can be expected, considering the experimental conditions and the assumptions made.

The earlier stages of extraction were interpreted in terms of the surface renewal theory ( § 4·3 ) It was assumed that, as a first approximation, results could be expressed in terms of a time mean rate of surface renewal $\bar{s}$, so that, from equation (5.7),

$$K_{lm} = \bar{F}(s,t) \cdot 2\sqrt{\frac{D_e}{\pi t}} \qquad (5\text{-}20)$$

whence $$K_{lm,Pr}/K_{lm,Ph} = \sqrt{D_{e,Pr}/D_{e,Ph}} \qquad (5\text{-}8)$$

Equation (5-8) was tested for the four lowest contact times. Table 5.3 shows that the deviation decreases with decreasing extraction.

Table 5.3: $x$ % Deviation, $\dfrac{K_{lm,Pr}/K_{lm,Ph} - D_{e,Pr}/D_{e,Ph}}{D_{e,Pr}/D_{e,Ph}}$

| Column Height | Re | t | $E_{Pr}$ | $E_{Ph}$ | % Deviation, |
|---|---|---|---|---|---|
| 5.2 cm | 14.7 | 1.0 | 0.784 | 0.589 | -5 |
| 2.2 cm | 4.6 | 0.68 | 0.825 | 0.615 | -11 |
| | 8.0 | 0.55 | 0.73 | 0.530 | -8 |
| | 14.7 | 0.42 | 0.66 | 0.490 | +1 |
| | | | Mean Deviation $\bar{x}$ | | -6.0 |

Figs. 5.3 and 5.4 are plots of $\bar{F}$ vs t and show a deviation between $\bar{F}_{Pr}$ and $\bar{F}_{Ph}$ decreasing with contact time. It is probable, judging from the results of Table 5.2, that the increased deviation at higher contact time can be resolved by assuming a different mechanism of mass transfer. Further evidence to support this view is given in § 5.4.

Figs. 5.5, 5.6 are log-log plots of $\bar{s}_{Ph}$ (from equations 5-20 and § 4.3a) vs. t. These plots are used for two reasons: firstly, because they seem to be linear, and thus afford a clearer comparison between the various runs; secondly, in order to give an idea of the variation of "mean rate of surface renewal", $\bar{s}$, with time. The lines can be represented by the following equations

$$0.2,0.04/0,0 \quad : \quad \bar{s} = 38\ Q_c\ t^{-1.3} \qquad 5.21$$

$0,0.2/0,0$ : $\bar{s} = 28Q_c t^{-1.3}$ (5.21a

$0,0.04/0,0$ : $\bar{s} = 30Q_c t^{-1.4}$ 5.21b

From comparison of equations (5.21) and (5.21b), it would seem that the effect of 0.2M acid on 0.04M phenol is to raise the coefficient of the phenol. The effects of mixing the solutes are shown in Table 5.4.

Table 5.4: $\bar{x}, \bar{F} = \frac{(\text{Mixed} - \text{Separate})}{\text{Mixed}} \bar{F} \times 100$

Mean values of $x$ taken from Appendix 2

| Run | n | $\bar{x}, \bar{F}_{Pr}$ | $\bar{x}, \bar{F}_{Ph}$ |
|---|---|---|---|
| $0.2,0.2/0,0$ | 3 | -4 | -1 |
| $0.2,0.04/0,0$ | 3 | +0.6 | +9.6 |
| $0.04,0.2/0,0$ | 3 | +2 | -2 |

The most pronounced effect is that of 0.2M acid in raising the coefficient of 0.04 M phenol. This effect is shown consistently in Fig. 5.6.

From the values of $\bar{s}$ at low t two points of interest emerge. Firstly, the values are high ($10 < \bar{s} < 100$); whereas, according to the theory of Scriven and Sternling (§ 1.8) transfer in this direction should not produce any interfacial disturbance, since solute is passing out of the phase ($CCl_4$) of both higher solute diffusivity and lower kinematic viscosity. Secondly, the values for propionic acid are higher than those for phenol;

whereas, from Figs 3.3, 3.4, phenol is the more surface active solute, and might be expected to produce a greater amount of interfacial disturbance. (Examination of Plates 5.1, 5.2 shows that in one way this is so: the phenol produces fewer eruptions but some of a much larger scale). An interpretation of these two anomalies is offered in § 5.9(iii).

5.4 Acid in $CCl_4$/Phenol in Water Runs 11.

Initial concentrations of the two phases were 0.2,0/0,0.05. The film phase was $CCl_4$.

Table 5.5 is similar to Table 5.3 in showing increasingly at lower contact times the agreement between the $K_{lm}$ ratio and the $\sqrt{D_e}$ ratio which would be expected to hold if the surface renewal theories were applicable.

Table 5.5: % Deviation, $\dfrac{\sqrt{D_{ePr}/D_{ePh}} - K_{lmPr}/K_{lmPh}}{\sqrt{D_{e,Pr}/D_{e,Ph}}}$

| t | 0.49 | 0.70 | 1.0 | 1.2 | 1.7 | 2.4 | 4.2 | 6.1 |
|---|---|---|---|---|---|---|---|---|
| $\varkappa$,% | +4 | -5 | $-\frac{1}{2}$ | +13 | -1 | +10 | -9 | +9 |

Table 5.5 also shows a closer agreement at longer times than do the results of § 5.3, (Figs. 5.3, 5.4). The probable reason is that since phenol is now in the water phase, and $m = C_c/C_w \doteq 0.5$ favours this phase,

the fractional extraction $E = (C_{c,o} - C_{c,t})/mC_{W,o}$ is now doubled, and $E_{Ph} \doteq E_{Pr}$; so that the errors due to taking the log mean driving force over the later stages of extraction are now about equal for both solutes.

Figs 5.7, 5.8 show $\bar{s}$ vs. t. Compared with the results of § 5.3, Fig. 5.7, it appears that there is in this case

(a) less difference between values at different flow-rates

(b) a lower initial value of $\bar{s}$ but a less rapid decrease of $\bar{s}$ with time.

5.5 Horizontal Extractor Runs 19 - 25

The results from the horizontal extractor are discussed here because they are similar to those in § 5.3, 5.4. Thus in Fig. 5.10 the addition of 0.2M propionic acid raises the coefficient for phenol, as in § 5.3; and the transfer of phenol from water to $CCl_4$ in opposition to the acid gives a lower initial value of $\bar{s}$ and a higher final value, as in § 5.4. However, a marked difference is that on testing the surface renewal equation

$$K_{lm,Pr}/K_{lm,Ph} = \sqrt{D_{e,Pr}/D_{e,Ph}}$$

the L.H.S. quantity is found to be about 20% too high, whereas if the initial driving force is used i.e.

$$K_{In,Pr}/K_{In,Ph} = \sqrt{D_{e,Pr}/D_{e,Ph}}$$

the L.H.S. is about 5% too low. (Table 5.6)

Table 5.6: % Deviation, $\dfrac{\sqrt{D_e \text{ ratio}} - K \text{ ratio}}{\sqrt{D_e \text{ ratio}}}$

| K | n | $\bar{X}$ | 95% Confidence Limits |
|---|---|---|---|
| Log. Mean D.F. | 10 | -19 | $(-19 \pm 20)\%$ |
| Initial D.F. | 12 | +4 | $(+4 \pm 4.2)\%$ |

In other words, the effective mean driving force is nearer to the initial value than to the log. mean value. Examination of plates 5 shows the presence of many density eddies. The graph of relative density of $CCl_4$ phase vs. solute concentration $C_c$ (fig. 3.5) confirms that the impoverished $CCl_4$ phase near the interface will tend to sink and be replaced by richer liquid from the interior. Thus the concentration of solute at the interface, and hence the driving force, could well be much closer to the initial value than if density eddies were absent. Thus it is probable that, within the above limits, equation (5.23) provides a valid basis of comparison for the two solutes.

Spontaneous interfacial disturbances were usually visible up to contact times of 100 seconds. From Figs 5.10, 5.11, the value of $\bar{s}$ is seen to be very much lower than for the vertical apparatus, and to decay more rapidly.

$$\bar{s} = A\, t^{-n} \qquad 1.5 < n < 4.5$$

Unfortunately the two ranges of contact times did not overlap, so no direct comparison is possible between the vertical and horizontal films.

Photographs: Plates 5.1 - 5.6 are schlieren photographs and plate 5.7 is a shadowgraph (§ 2.16).

Three points of interest are:

(i) The presence or absence of density eddies in the phases, depending on the direction of transfer, in accordance with the facts that the solutes make the $CCl_4$ phase lighter and the aqueous phase heavier. (vid. fig 3.5)

(ii) Since each solute produces nearly the same change of density with concentration, the strength of the density eddies is an indication of the rate of mass transfer and of the strength of the interfacial eruptions. The photographs agree with the values for $\bar{s}$ from the wetted wall column. Thus for transfer from $CCl_4$ to water, eruptions with acid are stronger than with phenol and decay less rapidly (plates 5.1, 5.2 and § 5.3); the weakest eruptions are those for transfer of acid out of water (plate 5.4 and § 5.6); those for transfer of phenol or of phenol and acid out of water seem to range between these extremes (plates 5.3, 5.6 and § 5.4, 5.7). On the whole, therefore, the photographs are consistent with the correlation of § 5.9(iii).

(iii) Plates 5.1 show the eruptions working against gravity, occasionally throwing the interfacial liquid upward more than 5 mm.; but the main activity is confined, as in plate 5.2, to within a zone 1 mm. on either side of the interface. The shadowgraph plate 5.7 shows intense eruptions confined to within 0.5 mm. of the interface.

In addition there is the curious flow pattern in plate 5.3. Concentration driving forces for mass transfer are in this case such that rate of phenol leaving water is little greater than rate of acid leaving $CCl_4$ so that the density differences produced by solute transfer almost balance. Filaments here are much finer than elsewhere, and it looks as if the interfacial movements which in fig 5.7 were confined to near the interface have been able to stir up larger masses of fluid without producing the familiar mushroom shaped density addies.

## 5.6 Phenol in $CCl_4$/Acid in Water

Runs 12.

Initial concentrations were 0, 0.05/0.5, 0. The high acid concentration gave a conveniently high value for $m_{i,Pr} \doteq 0.2$. The film phase was $CCl_4$.

Compared with §§ 5.3, 5.4, these are the first runs with acid in the water phase, and the lowest values of $\bar{s}$.

Bearing in mind that the acid has a distribution coefficient heavily weighted in favour of extraction from $CCl_4$ into water, the results suggest that distribution coefficient may have a considerable effect on the interfacial eruptions; a hypothesis which is supported by the considerations that the phenol distribution coefficient is less weighted in favour of water and also that

(a) from 5.3, for transfer from $CCl_4$ to water, $\bar{s}_{Pr} > \bar{s}_{Ph}$

(b) there is less disparity between transfer of phenol in the two opposite directions than between that of acid (see also § 5.7).

On comparing the mass transfer coefficients of the two solutes, it is seen that $\bar{F}_{Pr}$ is always lower than $\bar{F}_{Ph}$, (Table 5.7)

Table 5.7: $\chi$ % Deviation, $(\bar{F}_{Pr} - \bar{F}_{Ph})/\bar{F}_{Pr}$

| t | 0.49 | 0.70 | 1.0 | 1.2 | 1.7 | 2.4 | 2.4 | 3.5 | 4.0 | 5.3 | 6.3 | 9.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\chi$ | -18 | -21 | -16 | -10 | -16 | -20 | -23 | -9 | -24 | -11 | -1.5 | -23 |

Since in this case $E_{Pr} \approx E_{Ph} \approx 0.3$, the above results taken by themselves would argue seriously against the hypothesis that mass transfer coefficient is here directly proportional to $\sqrt{D_e}$. However, as shown in § 5.9 et sequ., the bulk of the evidence indicates that the above

low acid coefficients, $\overline{F}_{Pr} < \overline{F}_{Ph}$, is consistent with an interfacial resistance to transfer of acid in the direction water to $CCl_4$.

It may be noted (Figs. 5.5 - 5.8) that the effect of flowrate on $\overline{s}$ decreases progressively in the sequence of runs §§ 5.3, 5.4, 5.6. Reference to Table 5.1 shows this sequence to be one of decreasing fractional extraction E. Thus it is likely that the effect of flowrate is simply connected with the change of driving force due to extraction of solute. The higher flowrates have a lower fractional extraction at a given contact time, and thus maintain a higher rate of interfacial eruptions. With both solutes in the film phase, and a $CCl_4$ film, this effect would be most marked ( § 5.3) because of the combined effects of low distribution coefficient ($m < 0.5$) and low ratio of film liquid to bulk liquid flowrates (about 0.05).

## 5.7 Both Solutes in Water Phase

### Runs 13 - 18

Because of wetting difficulties ( § 2.5) these runs were performed on a water film.

Table 5.8 compares transfer of the separate solutes in the directions $CCl_4$ to Water, and Water to $CCl_4$

Table 5.8: Comparison of $\bar{s}$, (C → W) and (W → C).

| | | t = 2.9 | t = 8.8 |
|---|---|---|---|
| | ACID | $\bar{s}$ | $\bar{s}$ |
| C - W | 0.2,0/0,0 | 2.1 | 0.3 |
| W - C | 0,0/0.8,0 | 0.77 | 0.45 |
| C - W | 0.05,0/0,0 | 1.2 | |
| W - C | 0,0/0.05,0 | 0.02? | |
| | PHENOL | | |
| C - W | 0,0.2/0,0 | 2.0 | 0.35 |
| W - C | 0,0/0,0.2 | 0.80 | 0.39 |
| C - W | 0,0.05/0,0 | 1.5 | 0.2 |
| W - C | 0,0/0,0.05 | 0.80 | 0.03 |

It is seen that for both solutes higher values of $\bar{s}$ are obtained for transfer from $CCl_4$ to Water than from Water to $CCl_4$. According to the theory of Scriven and Sternling ( § 1.8) the opposite would be expected.

Comparison of separate with simultaneous transfer is given in Table 5.9.

Table 5.9: $\bar{F}$, (w → c)

| Acid | | Phenol | |
|---|---|---|---|
| Separate | Simultaneous | Separate | Simultaneous |
| 1.39 | 1.42 | 1.45 | 1.71 |
| 1.39 | 1.12 | 1.32 | 1.35 |
| 1.04 | 0.99 | 1.50 | 1.50 |
| 1.17 | 1.03 | 1.04 | 1.09 |

Comparison of the $\sqrt{D_e}$ ratio with the $\bar{F}$ ratio shows that the latter is consistently lower (Table 5.10)

Table 5.10: Simultaneous Transfer, (w - c)

| t | $\bar{F}_{Pr}$ | $\bar{F}_{Ph}$ | $\bar{F}$ ratio | $\sqrt{D_e}$ ratio | % Deviation |
|---|---|---|---|---|---|
| 2.9 | 1.42 | 1.71 | 1.11 | 1.34 | -17 |
| 8.8 | 1.12 | 1.32 | 1.21 | 1.43 | -10 |
| 2.9 | 0.99 | 1.50 | 1.00 | 1.58 | -37 |
| 8.8 | 1.03 | 1.55 | 1.03 | 1.58 | -34 |
| 13.8 | 0.80 | 1.09 | 1.15 | 1.57 | -22 |
| | | | 95% Confidence Limits | | -24 ±14 |

Fractional extraction is here only about 10% for each solute, so that these results are significant as a test - either of the applicability of the $\sqrt{D_e}$ ratio or of the presence of an interfacial resistance to transfer of acid from water to $CCl_4$. In an attempt to decide

between the two hypotheses, some runs were performed with surface active agent in the water phase, in order to suppress both waves and interfacial eruptions, and hence bring about a lower fractional extraction in the direction $CCl_4$ to Water. Under these conditions the penetration equations would apply, (5-1,-2), and $K_{In}$ ratio $= \sqrt{D_e}$ ratio.

5.8 Wetted Wall Column - Surface Active Agent in Aqueous Phase

Runs 26 - 30

A water film was used, with 0.05% v/v "Teepol 530". ( § 2.5).

Since eruptions and waves are absent, and E is low ($0.1 < E < 0.3$), the initial driving force coefficient $K_{In}$ is used, in accordance with § 4.1, (Equation 5-6). Table 5.11 shows a comparison of $\sqrt{D_e}$ ratio with $K_{In}$ ratio. (Mean values, drawn from Appendix 2).

Table 5.11: Mean Deviation, $\frac{\sqrt{D_e \text{ ratio}} - K_{In} \text{ ratio}}{\sqrt{D_e \text{ ratio}}}$

| Runs | n | $\bar{x}$ | Std Error | t - test | |
|---|---|---|---|---|---|
| C→W | | | | t | P |
| 26: 0.1, 0.1/0, 0 | 7 | +2 | 2.1 | 0.95 | > 0.1 |
| 27: 0.2, 0/0, 0.2 | | | | | |
| W→C | | | | | |
| 28: 0, 0/0.6, 0.3 | | | | | |
| 29: 0, 0.1/0.6, 0 | 6 | +9.5 | 1.5 | 6.3 | < 0.001 |
| 30: 0, 0.2/0.3, 0 | | | | | |
| (W→C) - (C→W) | From above =13 | +7.5 | $\sqrt{2.1^2+1.5^2}$ = 2.6 | 2.9 | 0.01 > P > 0.005 |

From Table 5.10 it is seen that for acid in the $CCl_4$ phase and phenol in either phase, (Runs 26 and 27), disagreement between the theoretical and experimental ratios is not significant. On the other hand, with acid in the aqueous phase and phenol in either phase, Runs 28, 29 and 30, disagreement is highly significant, as also is disagreement between the two sets of runs.

Since similar results were obtained in the absence of surface active agent, (§ 5.6), there are grounds for assuming that some specific factor causes a decrease in the rate of transfer of propionic acid from water to $CCl_4$.

The interfacial resistance could not be tested directly from equation (5-6) for the individual solutes, because the presence of surface active agent produced a tendency for inherent but hitherto negligible misalignments of the column B and cap C, (Fig. 2.2), to result in extreme ( 100%) differences of interfacial velocity around the periphery of the column. This effect accompanied the elimination of waves (q.v. § 2.7) which were found to even out velocity distribution around the perimeter of the column. Initial differences in velocity due to imperfections at the film inlet were possibly enhanced by the tendency of slower moving portions of the interface to be drawn into their faster moving peripheral neighbours because of differences in dynamic interfacial tension due to their different contact times, (§ 4.7), a process which would be self increasing. It was observed by means of dye particles (§ 2.8) that although the column was completely wetted, a large part of the liquid "short circuited" through locally thicker, faster moving strips of the film. However, it is likely that, within the experimental error, this phenomenon can be assumed to alter only the effective contact time t in equations (5-1, -2, -3), so that for simultaneous transfer the $\sqrt{D_e}$ ratio based on $K_{In}$ would still hold. The results of Table 5.10, (Runs 26,27), would seem to justify this

assumption, since they show agreement within 95% confidence limits of (+2 ± 5)%.

## 5.9 Review of Results.

The three main conclusions arising from examination of the experimental data are discussed below.

(i) According to the surface renewal theory of 4.3,a, simultaneous transfer of the two solutes should, under certain conditions - low E, constant s - take place in the ratio of the square roots of their effective diffusivities. Table 5.11 shows the agreement between theory and experiment for the vertical apparatus, with transfer of phenol in either direction but of propionic acid only from $CCl_4$ to water.

Table 5.11: % Deviation, $\frac{\sqrt{D_e \text{ ratio}} - K \text{ ratio}}{\sqrt{D_e \text{ ratio}}}$

Propionic Acid (C - W).

0.1 $E_{Pr}$ 0.85 ; 0.1 $E_{Ph}$ 0.5.

| Runs | $x$ |
|---|---|
| 7 | -8 |
| | -10 |
| | -2 |
| | -12 |
| 11 | -0.5 |
| | -5 |
| | +4 |
| 26 | -7 |
| | 0 |
| | -2 |
| | +8 |
| | +5 |
| 27 | +2 |
| | +9 |

Number of Observations n = 14

Standard Error $\sigma$ = 1.8

Mean Deviation $\bar{x}$ = -1.4

95% Confidence Limits = $(-1.4 \pm 3.9)\%$

Considering that the limits of error are no wider than the scatter in the original experimental data (e.g. Fig. 5.2), while they cover a fifteenfold range of contact time and mass transfer coefficient, a sixfold range of extraction, E, and a fourfold range of $m_{Ph}/m_{Pr}$, the relative constancy of the agreement shown is significant.

With the horizontal apparatus (§ 5.5) the same order

of agreement is found - (+ 4 ± 4.2)% - but in a more circumstantial fashion; namely, by assuming that the formation of density eddies caused the concentration of $CCl_4$ near the interface to be maintained at nearly its initial value, through replenishment by richer liquid from below. The presence of stronger density eddies in $CCl_4$ than in water was indicated by equilibrium density measurements (fig 3.5) and confirmed by schlieren photography.

The "mean rate of surface renewal" $\bar{s}$ was found to decrease with time according to the relation

$$\bar{s} = At^{-n} \qquad n \doteq 1.4$$

The decrease of $\bar{s}$ with t can be inferred qualitatively as follows.

Assume that the interfacial disturbances vary with the potential gradient, normal to the interface, of concentration and interfacial tension.

$$\text{i.e.} \quad s = Y\left(\frac{d\sigma}{dC} \cdot \frac{dC}{dy}\right)_i \qquad (5\text{-}23)$$

$$= Y\left(\frac{d\sigma}{dC}, C_A - C_{iA}\right) \qquad (5\text{-}24)$$

Hence, the interfacial disturbances will be self decreasing because they will tend to even out concentration gradients near the interface, both by mixing fluid from the interior with fluid at the interface, and by decreasing the mean concentration through increased mass transfer across the interface,

$$\text{i.e.} \quad \frac{d(C_A - C_{iA})}{dt} = - Y_2 (S, C_A - C_{iA})$$

whence, from the above,

$$\frac{ds}{dt} = - Y_3 (s) \qquad (5\text{-}25)$$

The experimental results can not give much information about the variation of $\bar{s}$ with t because usually only with the two lowest contact times of any run was the interface completely covered with eruptions. (v. § 5.3, and Plates). However, the log-log plots of $\bar{s}$ vs t give remarkably straight lines, (Figs. 5.5 - 5.8).

(ii) Transfer of propionic acid from water to $CCl_4$ resulted in

$$K_{Pr}/K_{Ph} < \sqrt{D_{e,Pr}/D_{e,Ph}}$$

whatever the direction of phenol transfer, and with or without surface active agent, (Table 5.12). Thus there are grounds for supposing that this deviation signifies the presence of a specific interfacial resistance to acid transfer in this direction.

Table 5.12: $\times$ % Deviation, $\frac{\sqrt{D_e \text{ ratio} - K \text{ ratio}}}{\sqrt{D_e \text{ ratio}}}$

Wetted Wall Column, Acid (C → W)

$0.1 < E < 0.3$

| Runs | Phenol Direction | $\times$ | $K_i^{-1}$ |
|---|---|---|---|
| 12 | (C → W) | +18 | 30 |
| | | +21 | 27 |
| | | +16 | 16 |
| 13 | (W → C) | +17 | 57 |
| | | +10 | 67 |
| 14 | (W → C) | +37 | 140 |
| | | +34 | 230 |
| | | +22 | 220 |
| 28 | (W → C) | + 9 | 48 |
| | | +10 | 58 |
| | | + 9 | 63 |
| 29 | (W → C) | + 8 | 55 |
| | | +13 | 68 |
| 30 | (C → W) | + 8 | 160 |

$n = 14$

$\sigma = 2.2$

t - test, $P < 0.001$

The magnitude of this resistance was estimated by

means of the equation for resistances in series

$$\frac{1}{K_i} = \frac{1}{K_{obs}} - \frac{1}{K_{calc}} \qquad (5\text{-}26)$$

which leads to the approximation

$$K_i^{-1} = \alpha \cdot K_{obs.}^{-1} \qquad (5\text{-}27)$$

whence

$$K_i^{-1} \approx 70 \text{ sec/cm, from Table 5.12.}$$

This value is just small enough to have escaped detection by Gordon and Sherwood, (§ 1 - 6), but is orders of magnitude smaller than the other values reviewed in chapter 1.

An idea of the physicochemical significance of such a resistance may be gained by the following approximations. Suppose the interfacial region is $10\text{Å}^{\circ}$ thick, then it has a permeability coefficient

$$K^{-1} = \frac{10\text{Å}^{\circ}}{D} = \frac{10^{-7}}{10^{-5}} = 10^{-2} \qquad (5\text{-}28)$$

The actual interfacial permeability coefficient, from Table 5.12, is

$$K_{obs.}^{-1} = 70 \doteqdot 10^{2}$$

(Net number of molecules which actually pass through the interfacial zone)

$\doteqdot$ (Net number which should normally pass through)

$$\frac{n}{n_o} = \frac{K_{obs}}{K} = \frac{10^{-2}}{10^{+2}} = 10^{-4} \qquad (5\text{-}29)$$

By the Boltzmann distribution law, assuming that the

molecules n have been active enough to surmount an energy barrier, $\Delta G$,

$$\frac{n}{n_o} = \exp\left(-\frac{\Delta G}{RT}\right) \qquad (5\text{-}30)$$

whence $\Delta G$ = 5000 cals/mol.

This value is not inordinately high. It is possible that the resistance is due to hydrogen bonding between acid and water, and the strength of an - H ··· O= bond is about 7000 cals [35]. However, MAIER [35] measured the activation energy for breaking the hydrogen bonds of benzoic acid dimers in $CCl_4$, and found it to be nearly 7,000 cals/bond. Thus the assumed mechanism by which hydrogen bonds would retard acid from leaving the aqueous phase must also explain why there is no equivalent resistance to the dimers on leaving the $CCl_4$ phase. An obvious difference between the two cases is that molecules of carboxylic acid in water are bonded to the solvent phase, whereas in $CCl_4$ they are bonded only to themselves. Therefore it is probably more difficult for monomer to leave the water than for dimer to leave the $CCl_4$. A further difference is that, having crossed the interfacial zone, dimers encountering the large excess of water would split at a net rate faster than the equivalent monomers entering the $CCl_4$ phase could contact each other and dimerize, which may explain the apparent

fivefold increase in resistance for Runs 14, which accompanies a fortyfold decrease in $C_{ic}$ compared to the other concentrations in Table 5.12.

However, another possible factor is that the method of calculating interfacial concentrations from equation (4-6) is inaccurate, giving values of $C_{ic}$ about 50% too high and thus $m_{iPr}$ about 20% too high because of the relatively steep change of $m_{Pr}$ with concentration compared to $m_{Ph}$; this would show up as an erroneously large driving force $mC_{W,o}$. But it is difficult to discuss this possibility because of the theoretical basis of equation (4-6).

(iii) The apparent strength of the spontaneous interfacial disturbances as measured by their effect of increasing the mass transfer coefficient - i.e. by $\bar{F}$ - is not explained by the theory of Scriven and Sternling, (1.8).

(a) Firstly the effects are strongest when solute is leaving the phase ($CCl_4$) of both higher solute diffusivity and lower kinematic viscosity - a result in direct opposition to their criterion of stability.

(b) Secondly, their expression for the growth of disturbance contains a scaling factor

$$\left( \frac{\partial \sigma}{\partial C} \cdot \frac{\partial C}{\partial y} \right)_i = A \qquad \text{dyne/cm}^2$$

From equations (4-3, 4-16)

$$\left(\frac{\partial C}{\partial y}\right)_{i,A \text{ or } B} = \frac{(C_A - mC_B)}{D_{A \text{ or } B}} \sqrt{\frac{D_e}{\pi t}}$$

Table 5.13: $\left(\frac{\partial \sigma}{\partial c} \cdot \frac{\partial C}{\partial y}\right)_i$ for $\pi t = 1$

$\bar{s}$ for $t = 29$

| | 0.2,0/0,0 | 0,0.2/0,0 | 0,0/0.8,0 | 0,0/0,0.2 |
|---|---|---|---|---|
| $\bar{s}$ | 2.3 | 2.0 | 0.8 | 0.8 |
| A | 6,000 | 2,500 | 1,000 | 2,300 |
| | 0.05,0/0,0 | 0,0.05/0,0 | 0,0/0.05,0 | 0,0/0,0.05 |
| $\bar{s}$ | 1.1 | 1.5 | 0.08 | 0.8 |
| A | 6,000 | 1,900 | 50 | 1,800 |

From table 5.13 and fig. 5.12 it appears that the size of $\bar{s}$ corresponds roughly to that of A.

The above considerations prompt the view that (a) vigorous and sustained eruptions may be initiated by movements of interfacial fluid (e.g. waves, density eddies, entry disturbances) in systems which might otherwise be stable

(b) the strength of eruptions for transfer in either direction is largely influenced by the same factors as affect ease of mass transfer - namely, m and $\sqrt{D_e}$.

Suppose that the freshly contacted system has an interfacial concentration $C_{iA,o}$.

Suppose now that some disturbance causes a re-contact of liquid in the interfacial zone. The new interfacial concentrations will be bounded by the two extremes

$$\text{(i)}\quad C_{A,o} + C_{B,o} \rightarrow C_{iA,R} = mC_{iB,R} \qquad (5\text{-}1)$$

$$\text{(ii)}\quad C_{iA,o} + C_{iB,o} \rightarrow C_{iA} = mC_{iB} \qquad (5\text{-}31)$$

Table 5.14 and fig 5.13 show the comparison between $(\Delta\sigma - \Delta\sigma_R)$ and $\bar{s}$, where the two interfacial pressures refer to the above concentrations, and $\bar{s}$ is for $t = 2.86$. This correlation is seen to be closer than that between $\bar{s}$ and $\frac{\partial \sigma}{\partial c} \cdot \frac{\partial c}{\partial y}$ in Fig. 5.12.

Table 5.14: $\Delta\sigma - \Delta\sigma_R$ / $\bar{s}$ for $t = 2.86$

| | Acid Alone | | | | Phenol Alone | | | |
|---|---|---|---|---|---|---|---|---|
| $C_{C,o}$ | 0.2 | 0.05 | 0 | 0 | 0.2 | 0.05 | 0 | 0 |
| $C_{W,o}$ | 0 | 0 | 0.8 | 0.05 | 0 | 0 | 0.2 | 0.05 |
| $\Delta\sigma - \Delta\sigma_R$ | 5.0 | 3.5 | 2.0 | 0.5 | 7.0 | 2.5 | 4.0 | 3.0 |
| $\bar{s}$ | 2.3 | 1.1 | 0.8 | 0.07 | 2.0 | 1.5 | 0.8 | 0.8 |

| | 0.2,0.05/0,0 | 0.05,0.2/0,0 | 0,0/0.8,0.2 | 0,0/0.05,0.0 |
|---|---|---|---|---|
| $\Delta\sigma - \Delta\sigma_R$ | 6.5 | 6.3 | 4.0 | 1.5 |
| $\bar{s}$ | 2.1 | 1.8 | 1.3 | 0.8 |

| | 0.2,0.2/0,0 | 0.2,0/0,0.05 | 0,0.05/0.5,0 |
|---|---|---|---|
| $\Delta\sigma - \Delta\sigma_R$ | 6.5 | 6.5 | 4.5 |
| $\bar{s}$ | 1.9 | 2.6 | 1.5 |

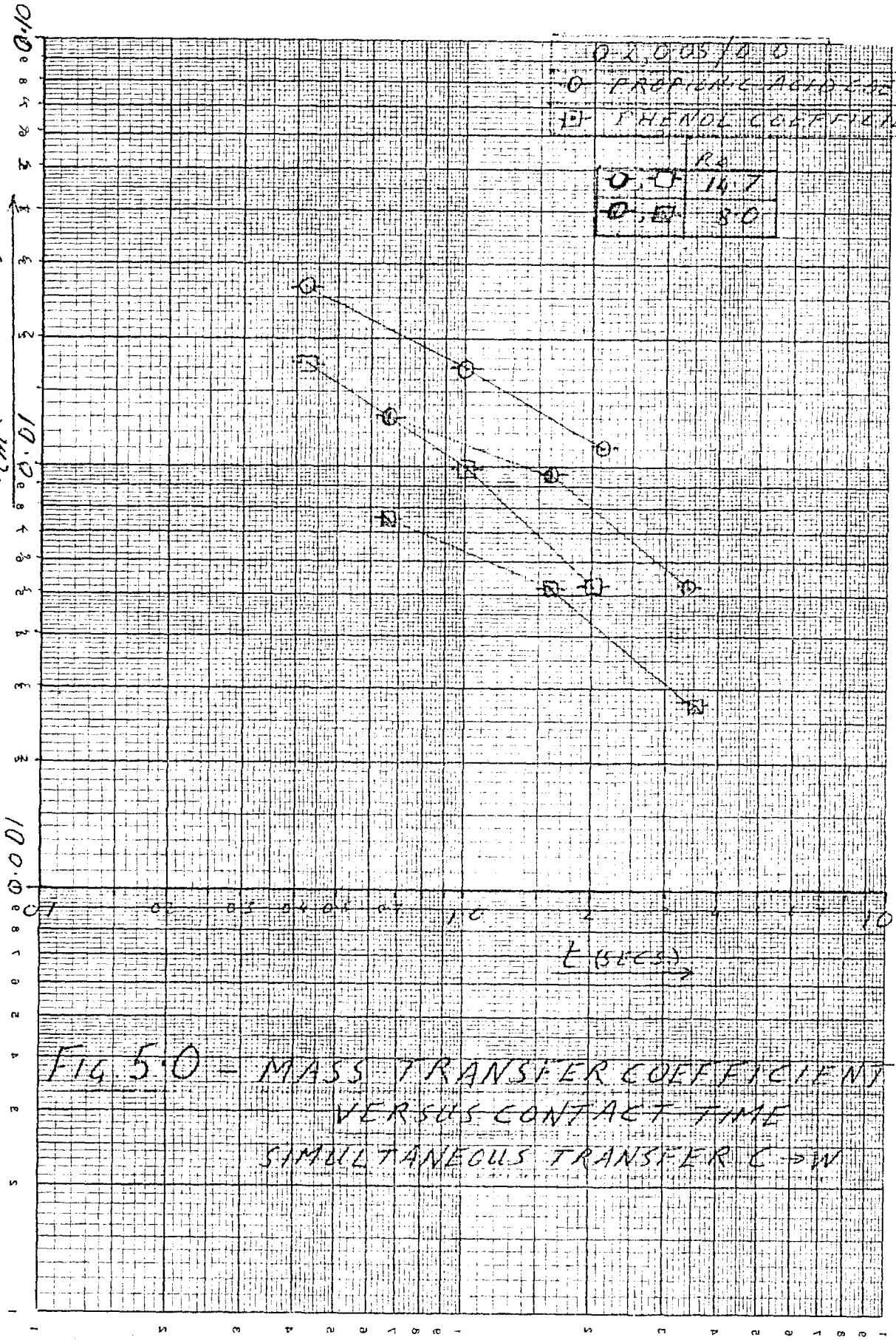



FIG. 5.0 – MASS TRANSFER COEFFICIENT VERSUS CONTACT TIME SIMULTANEOUS TRANSFER C → W

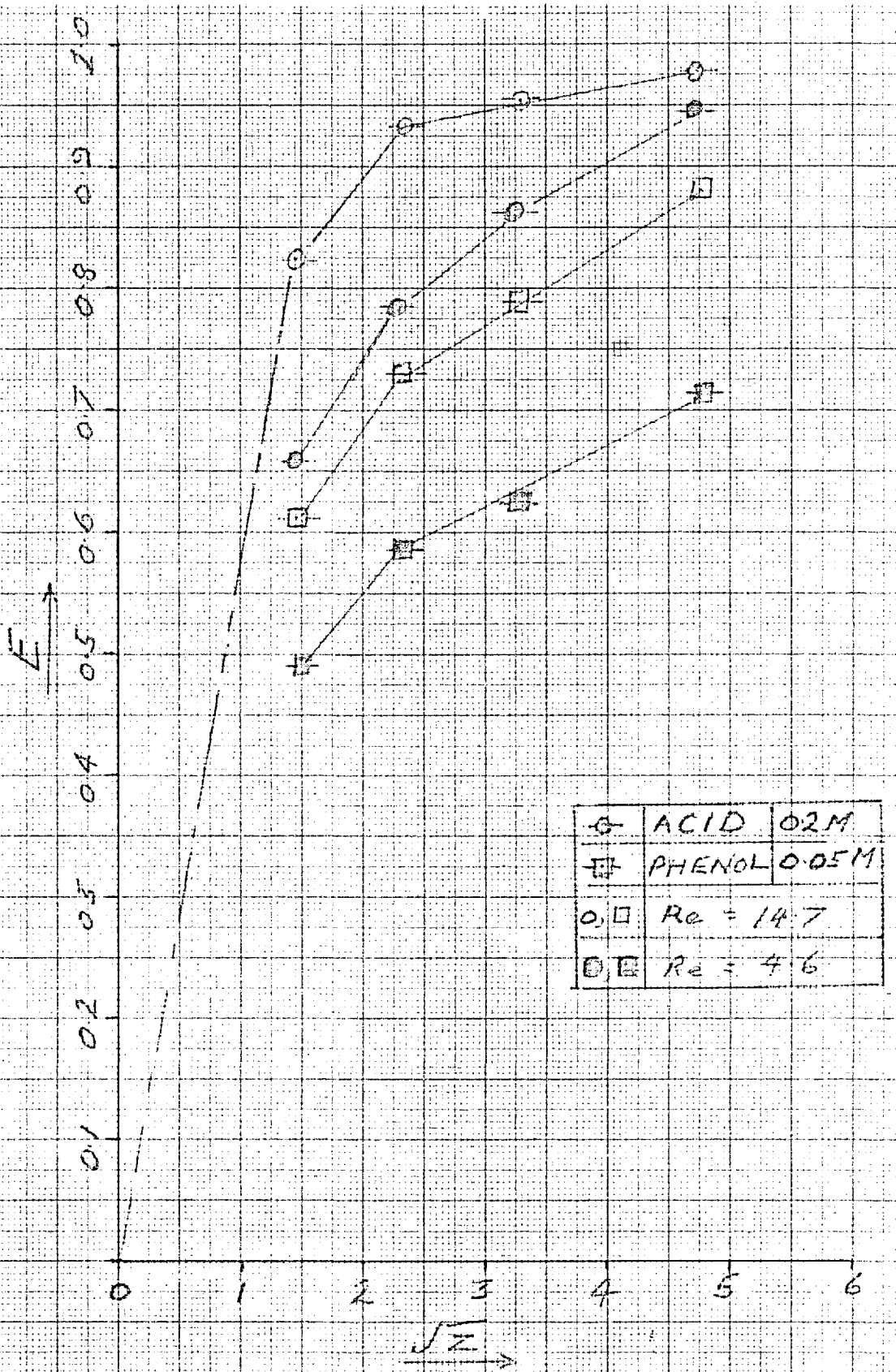



FIG. 5.1 – FRACTIONAL EXTRACTION AS A FUNCTION OF COLUMN HEIGHT

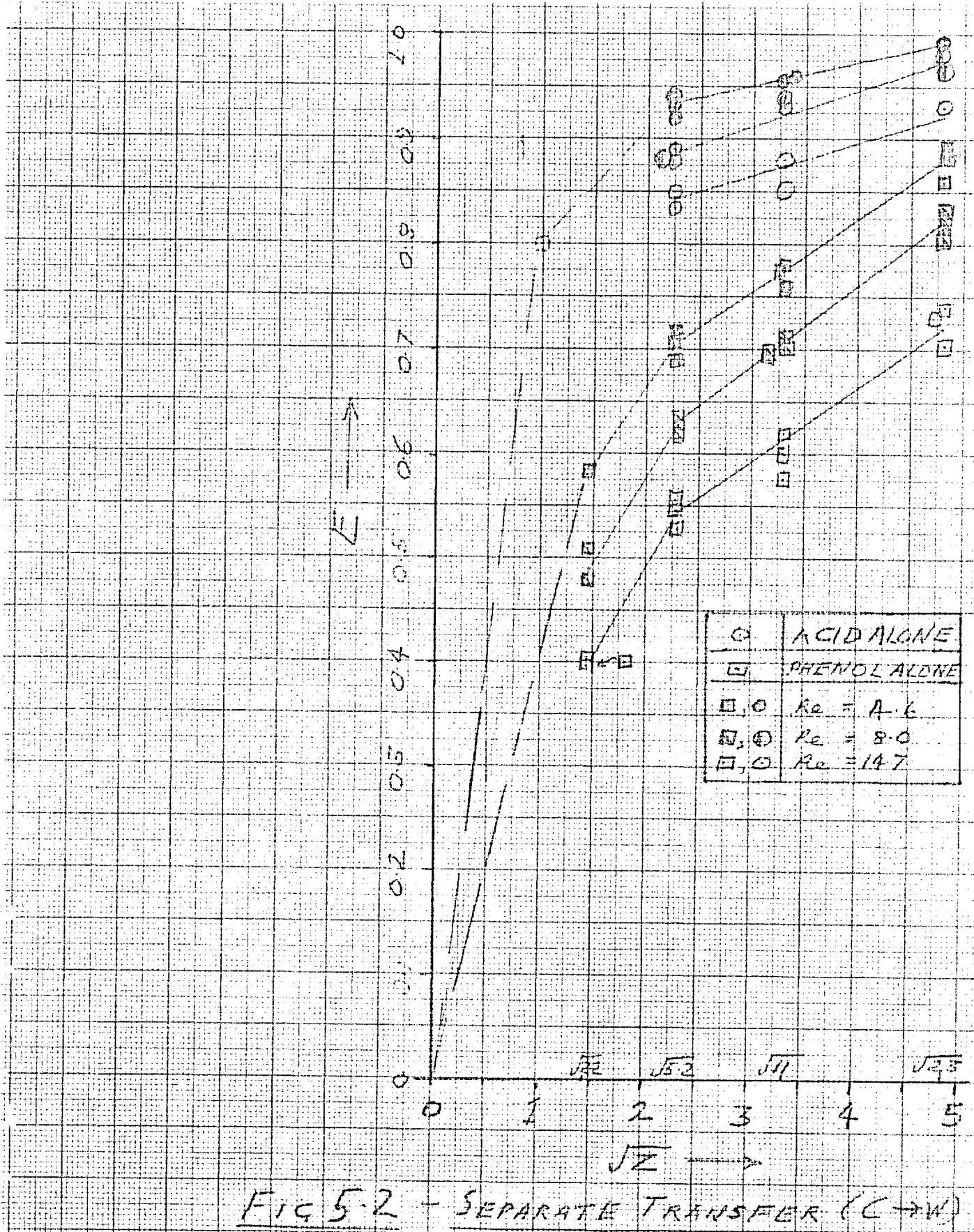



FIG 5.2 – SEPARATE TRANSFER (C → W)

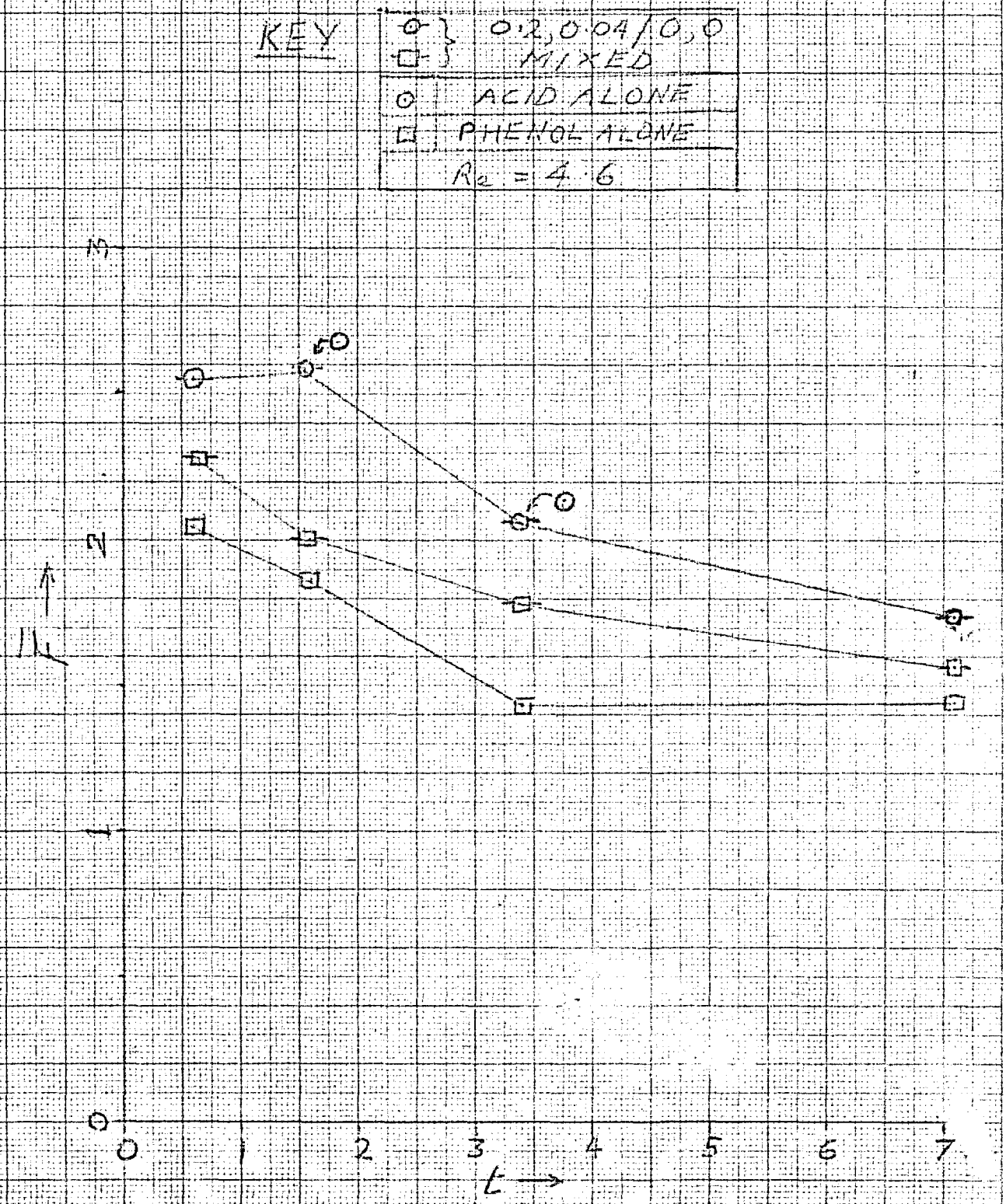



FIG 5·3 – SIMULTANEOUS AND SEPARATE TRANSFER C→W.

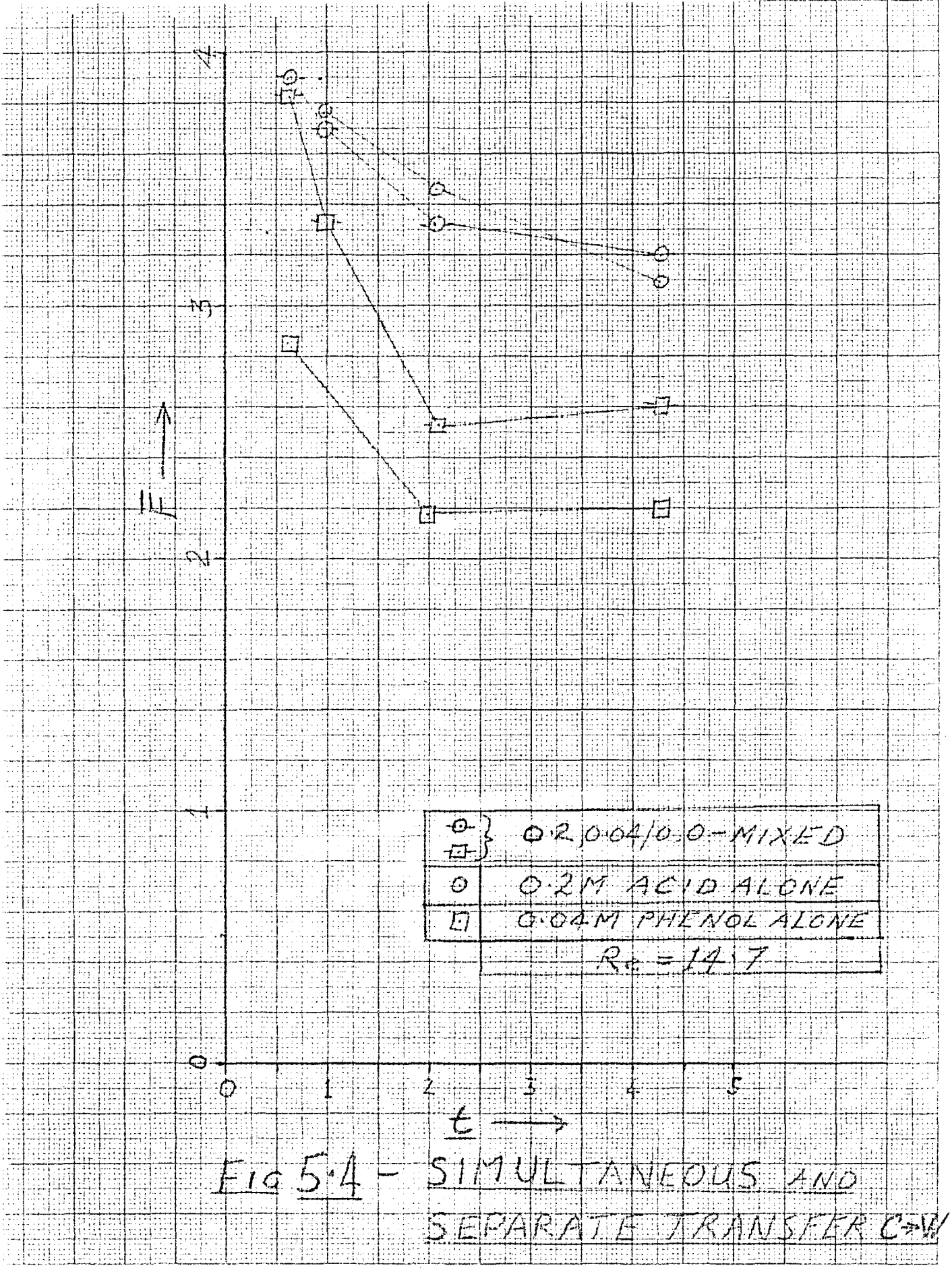



FIG 5·4 – SIMULTANEOUS AND SEPARATE TRANSFER C→W

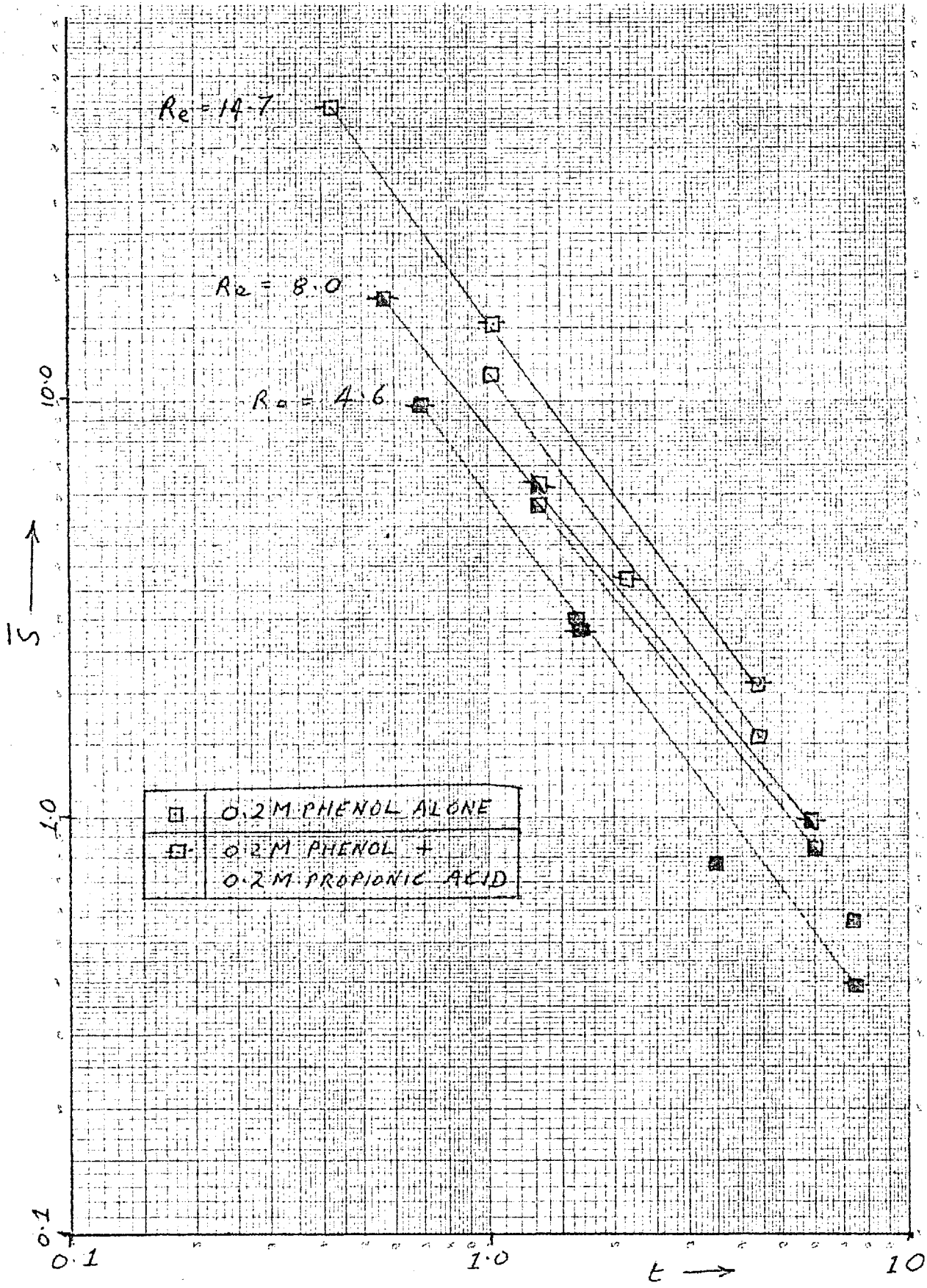



FIG 5·5 - SEPARATE AND SIMULTANEOUS TRANSFER OF 0·2 M PHENOL C → W

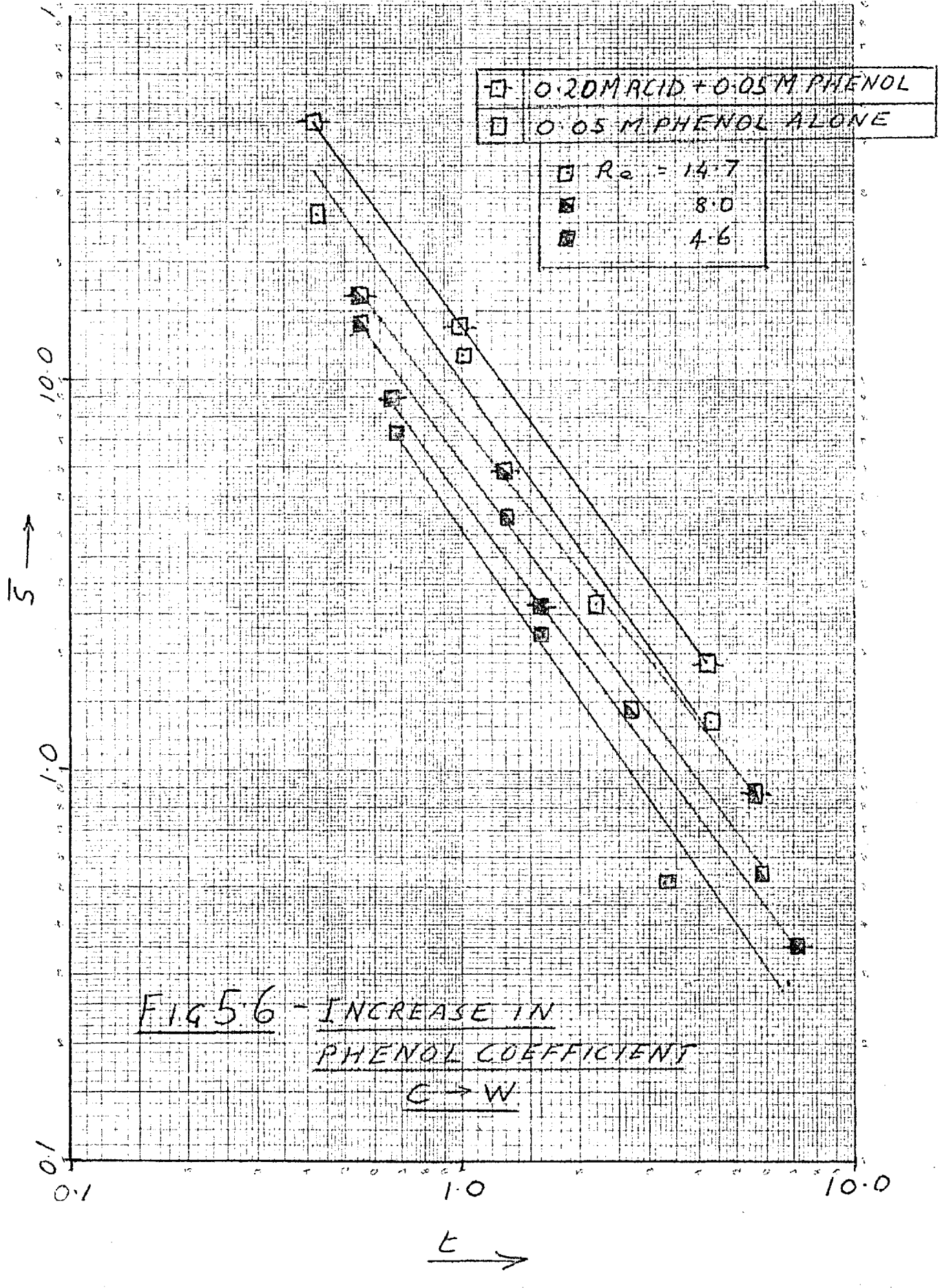



FIG 5·6 - INCREASE IN PHENOL COEFFICIENT C → W

DUPLICATED AS RECEIVED. CODE 1 CONTAINS CODE X 1 CM.

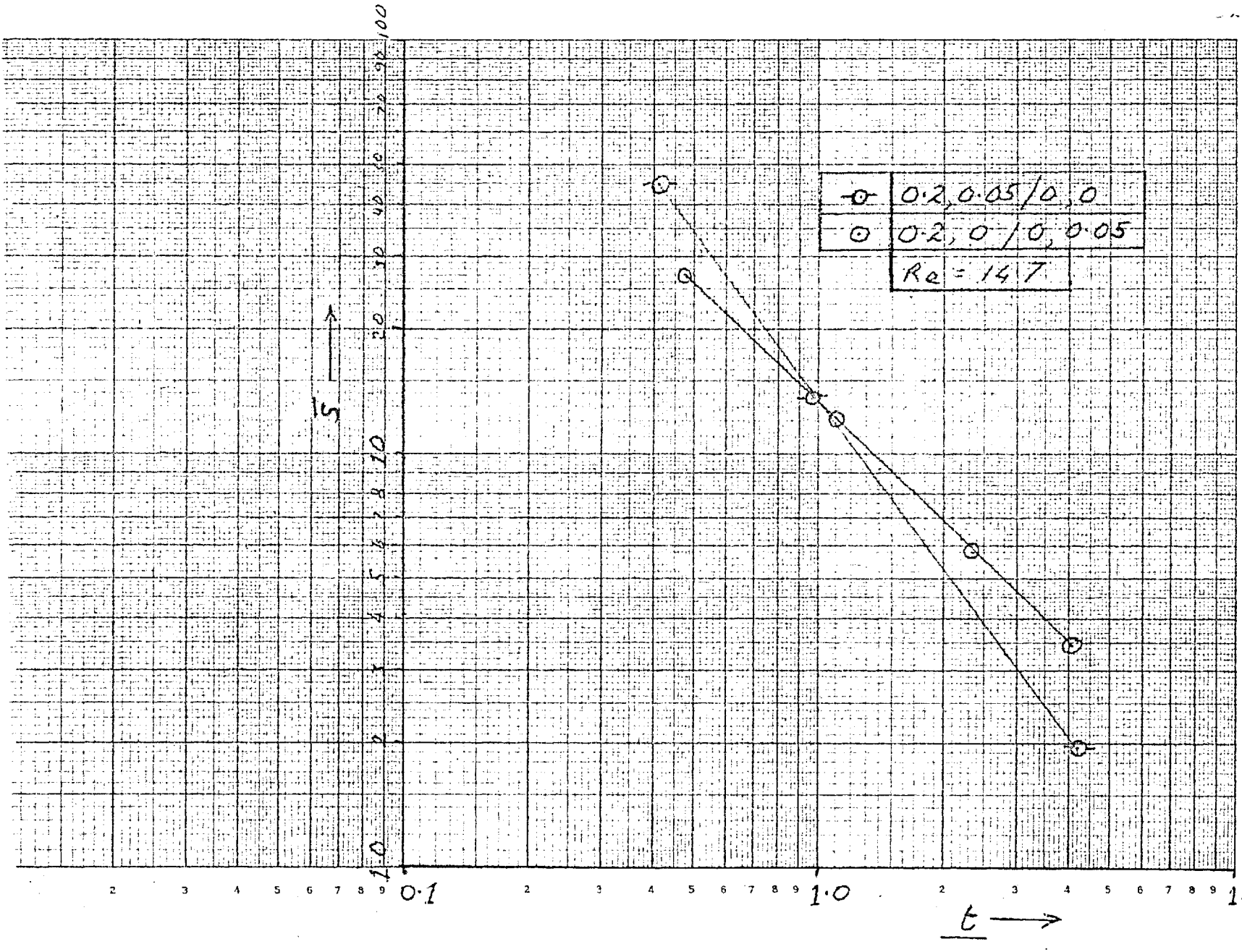



FIG 5·7 – COMPARISON OF 0·2, 0·05/0, 0 WITH 0·2, 0/0, 0·05

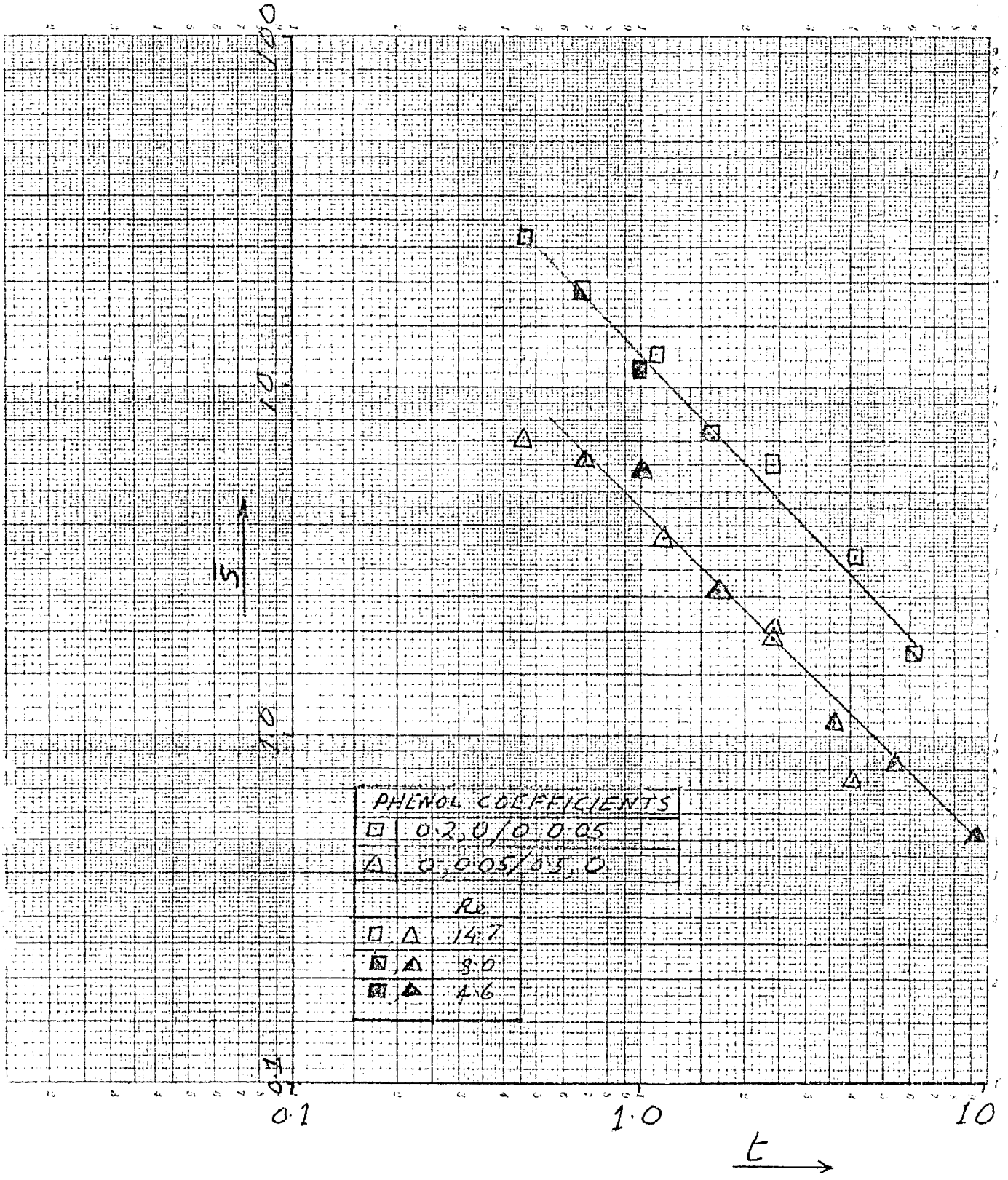



FIG. 5·8 - TRANSFER IN OPPOSITE DIRECTIONS

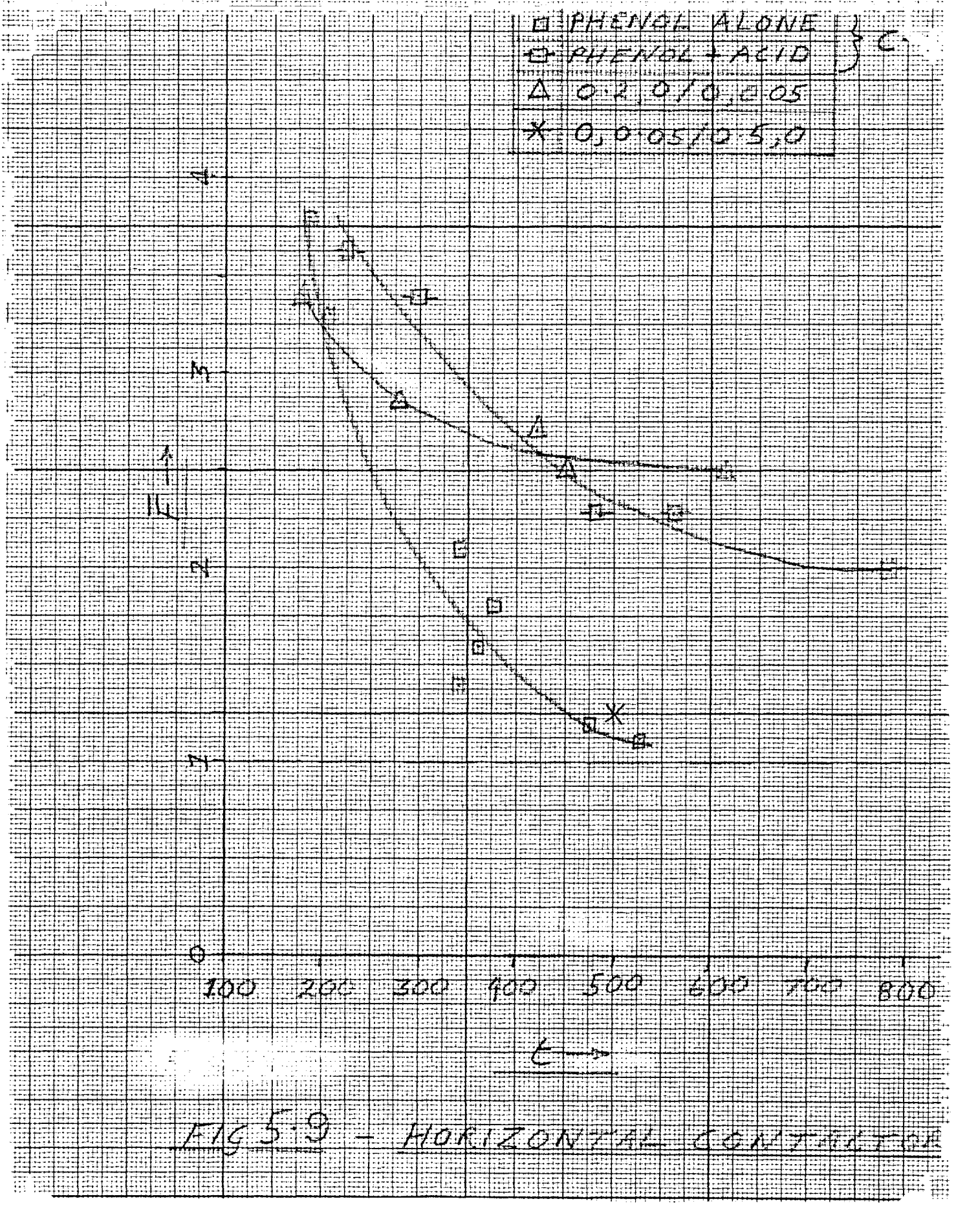



FIG 5.9 – HORIZONTAL CONTRACTION

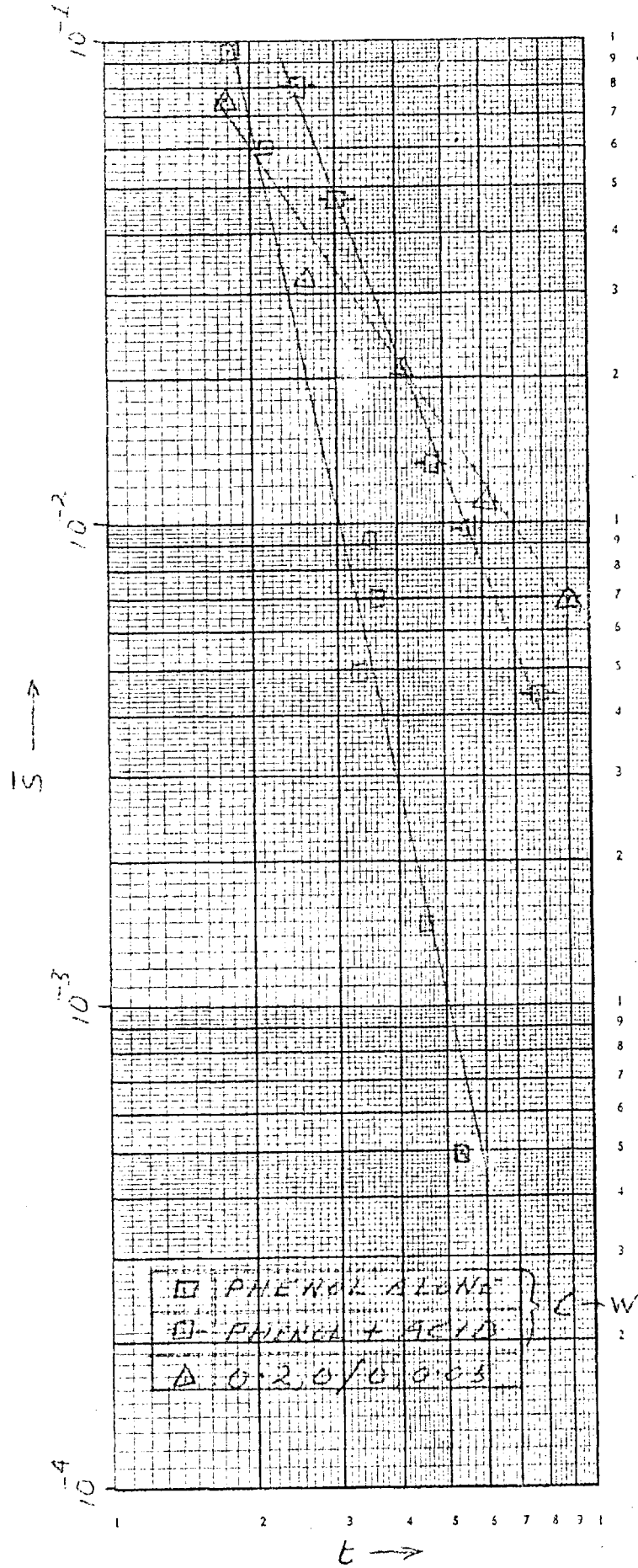



FIG. 5·10
HORIZONTAL
CONTACTOR

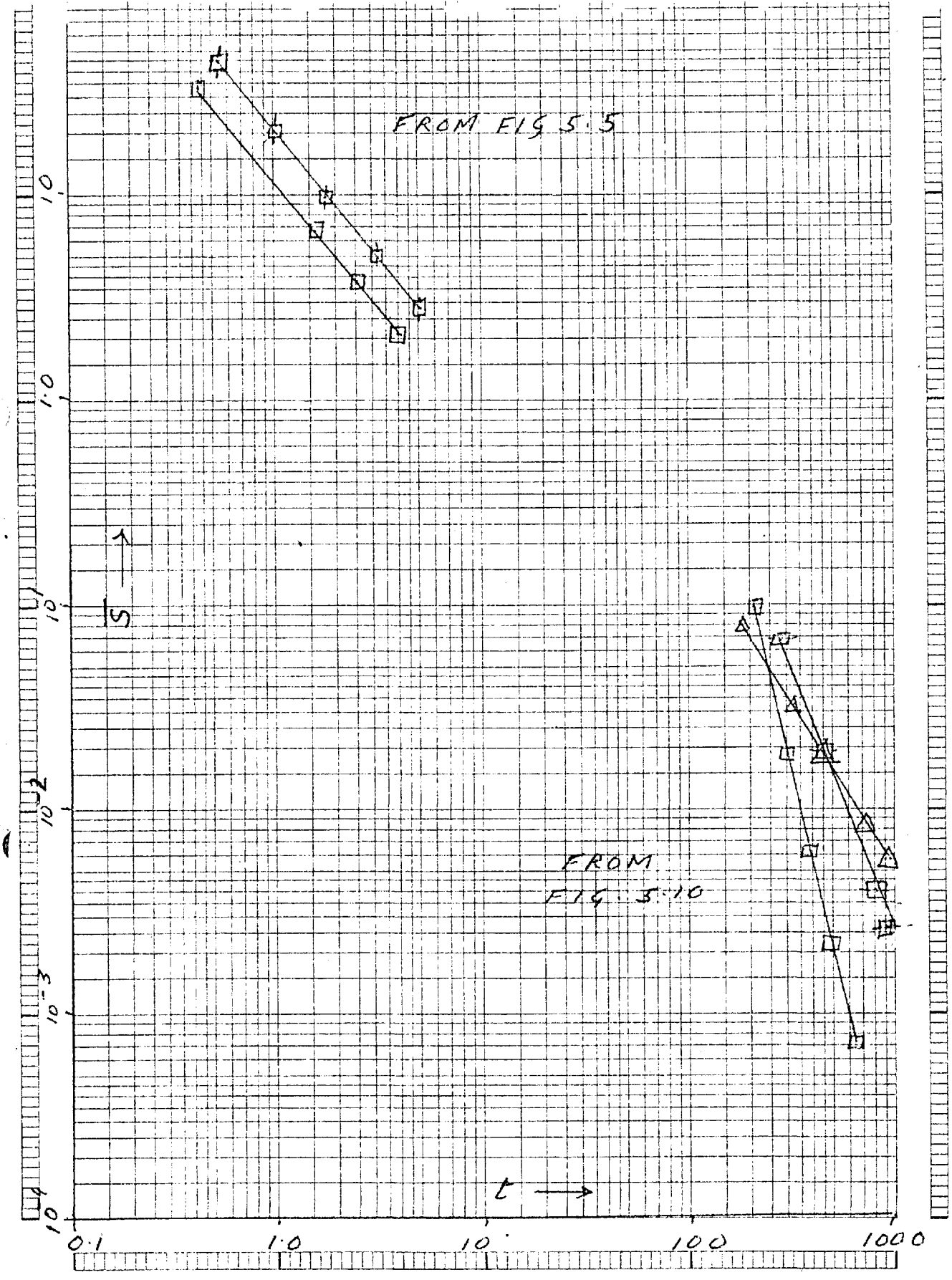
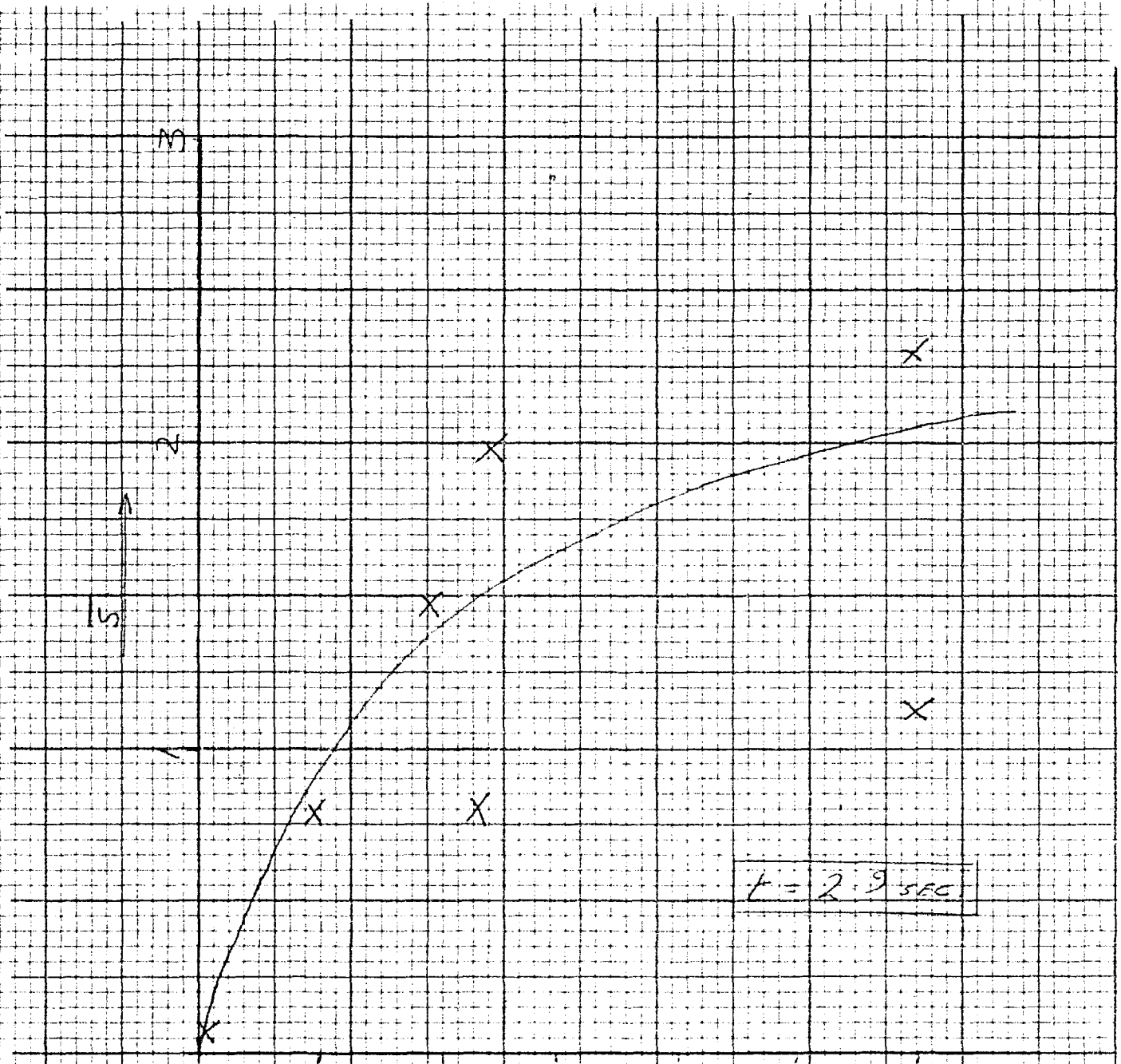



FIG 5·11 - HORIZONTAL AND VERTICAL CONTACTORS COMPARED




$$A = \left(\frac{\partial \sigma}{\partial C} \cdot \frac{\partial C}{\partial y}\right)_i \quad \text{DYNE CM}^{-2}$$

FIG 5·12 - CORRELATION OF ERUPTION WITH POTENTIAL GRADIENT OF INTERFACIAL TENSION

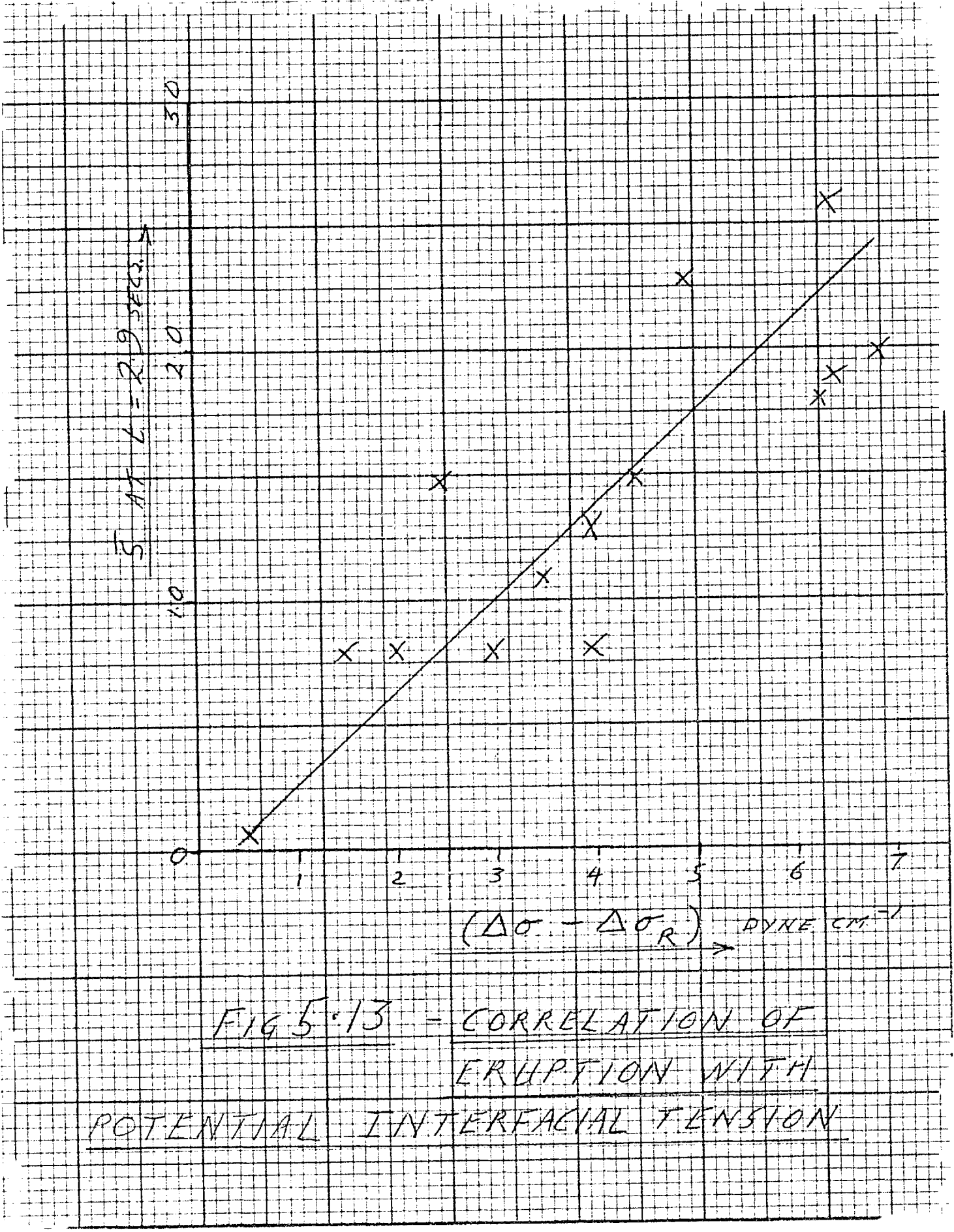



FIG 5·13 = CORRELATION OF ERUPTION WITH POTENTIAL INTERFACIAL TENSION




(a) 0-25 SECONDS



(b) 0-25 SECONDS



(c) 30-60 SEC.

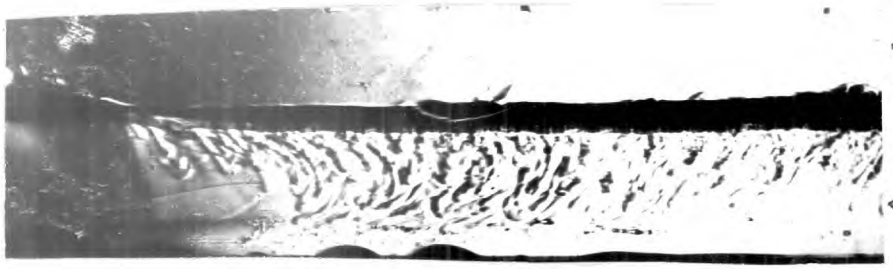



(d) 80-110 SEC.

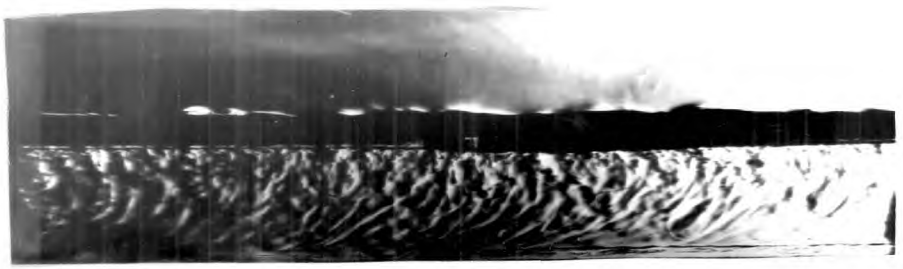
0, 0·2/0, 0 3X

PLATES 5·1

PHENOL C → W



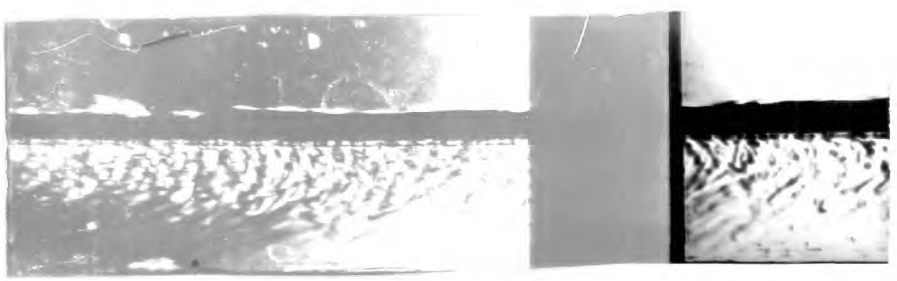

(a) 0 - 16 SECONDS



(b) 16 - 32



(c) 40 - 56



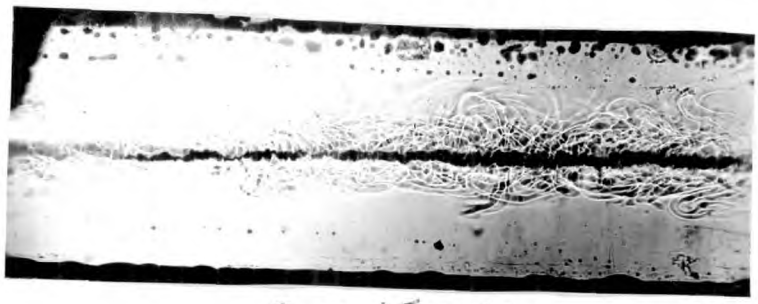
(d) 60 - 76

X 3

0·2, 0/0, 0

PLATES 5·2

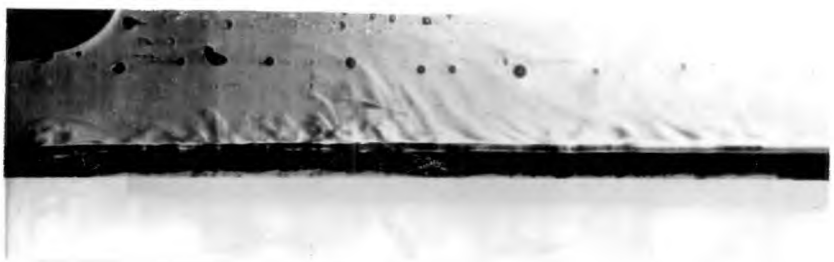
TRANSFER OF ACID C → W



5·3

0·05, 0/0, 0·2

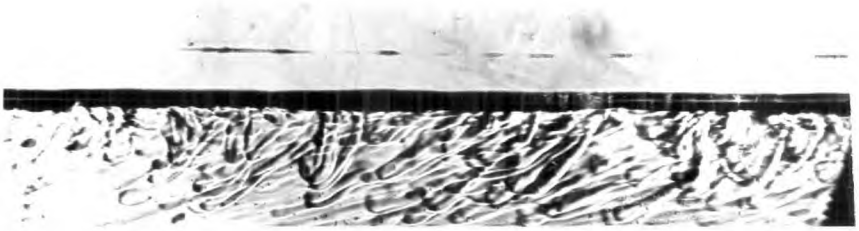
0 – 15 SEC 3X



5·4 ×3

0, 0·05/0·5, 0

0 – 16 SEC



5·5 ×3

0·2, 0/0, 0·2

44 – 60 SEC.

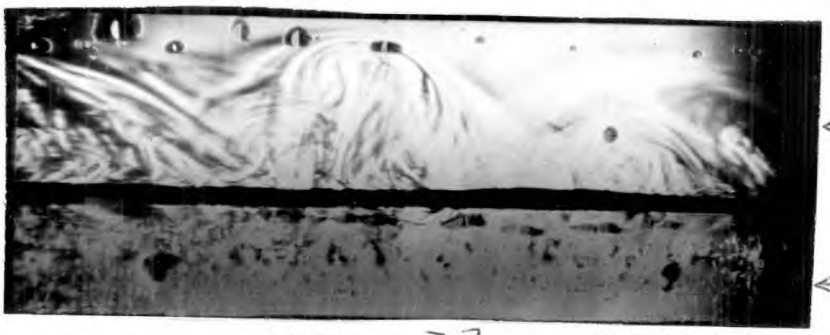


5·7 X5

0·2, 0·2/0, 0

(SHADOW GRAPH)

25 – 37 SEC.




20 - 32 SECONDS



x3

40 - 56 SEC

0,0 / 0,0·2

TRANSFER OF PHENOL W → C

PLATES 5·6

## CONCLUSION

Results from the vertical apparatus indicated the presence of interfacial eruptions which decayed with time. These phenomena were confirmed by visual observation on the horizontal apparatus. The schlieren photographs from the horizontal apparatus (plates 5) also confirm the mass-transfer results from the vertical apparatus, which indicated that the eruptions of the propionic acid are stronger than those of phenol when both solutes are transferred from $CCl_4$ to water, and vice versa for transfer from water to $CCl_4$; they also confirm that the most vigorous eruptions occur during transfer of propionic acid from $CCl_4$ to water, and the least vigorous during transfer of the same solute out of the water phase into the $CCl_4$.

Quantitative results for the transfer of propionic acid out of $CCl_4$ into water only, but with transfer of phenol in either direction, on the wetted wall column with and without surface active agent (§§ 5.3, .4, .8) confirm that the ratio of mass transfer coefficients for simultaneous transfer of the two solutes is equal to the effective diffusivity ratio as defined in § 5.1(b). Results from the horizontal apparatus confirm this ratio, provided that the initial driving force is used, for reasons substantiated by the schlieren evidence of strong

density eddies (§ 5.5). Since this ratio is the same whether or not interfacial disturbances (including waves) have been suppressed by addition of surface active agent, the above results support the interpretation of mass transfer under conditions of interfacial eruption in terms of the DANCKWERTS theory of fractional surface renewal.

For the transfer of acid out of water, with transfer of phenol in either direction, (§§ 5.6, .7, .8), it is argued that the low ratio of $K_{Pr}/K_{Ph}$ obtained is due to a specific interfacial resistance to transfer of acid in this direction; and the magnitude of this resistance, $K_i^{-1} = 70$, is consistent with the presence of strong hydrogen bonding between the acid molecules and the aqueous phase, (§ 5.9ii).

The schlieren photographs from the horizontal apparatus show the decay of interfacial eruptions with time (plates 5 ) as predicated by the interpretation of results from the wetted wall column. The shadowgraph of the interfacial region (plate 5.7) shows that "interfacial turbulence" (as opposed to the resultant density eddies shown in the schlieren photographs) is confined to a zone within one or two mm. of the interface, as was observed by WARD and BROOKS [1].

Values of the "average fractional surface renewal

rate" $\bar{s}$ from $10^{-3}$ to $10^{2}$ were recorded. These values can not be explained by the linearized stability theory of SCRIVEN and STERNLING (§ 5.9iii). They were better correlated (fig. 5.13) with a potential driving force ($\Delta\sigma - \Delta\sigma_R$) representing the difference in interfacial pressure between two neighbouring patches of the interface which have had different degrees of surface renewal as a result of extraneous disturbances such as entry shocks, waves or density eddies. There is some confirmation of the suggestion put forward at the end of § 4.9 that the effect of dynamic interfacial tension in suppressing the initiation of surface renewal would result in a lower eruptivity for the more surface active solute, phenol - again a result which could not be predicted from the equations of SCRIVEN and STERNLING (vid. equ. (4-49) of § 4.8).

## Suggestions for Further Work

It is an advantage of the method of simultaneous transfer of two solutes that it can be used as a check on theories of interfacial mass transfer in some cases where the hydrodynamics are uncertain. The method also has some practical interest as a means of fractional separation. Neither of these aspects have been much investigated.

Also of practical interest is the effect of interfacial eruptions in raising the mass transfer coefficient by as much as a factor of four (fig. 5.4). It would be of theoretical interest to know if there were an upper limit to this effect at very short contact times - perhaps by use of a jet contactor - and also to know more of the behaviour of $\bar{s}$ with such variables as solute - solvent properties, film thickness, concentration driving force, direction of transfer and presence of extraneous disturbances.

Each apparatus used in the present work had severe limitations, but both seem capable of further improvement. The lowest contact time of the wetted wall column was subject to the excessive growth of waves and end effect at

$$Z < 2 \text{ cm} \quad , \quad Re > 15$$

Use of surface active agents to suppress waves could

lower the contact time and hence increase the possibility of detecting interfacial resistances; however, as described in § 5.8, great care will be needed with centring, verticality and finish of the column and cap in order to obtain reproducibility comparable with that for gas liquid systems (§ 2.2).

The horizontal apparatus proved useful for observational purposes, but tended to instability because of the ease with which interfacial tension effects produced stagnancy, backmixing or short-circuiting of the interface and its associated fluid. The use of a fixed, rather high flow-rate may be an improvement, with the contact time being varied by varying the length (§ 2.13).

The tendency of the interface to move either faster or slower than it would if in a parabolic velocity profile has been observed in both apparatus, but not quantitatively studied. Recently SCRIVEN put forward general equations for the dynamics of a fluid interface in which the interface assumes complicated shapes, which may be of some value in describing the behaviour of the horizontal contactor; although his equations do not take into account the backpressure due to build-up of interfacial agents. It would be of interest to know how far these effects are present in packed columns; not only because of their influence on the steady state

mass transfer efficiency of the column, but also because, from the point of view of control, the response of a column to changes of inlet concentration may well be considerably different in a column where there is frequent fresh contact between the two phases from the response where most of the contact is across an old or a stagnant interface.

# APPENDIX 1

## 2.9 Flow Calculations for the Wetted Wall Column.

Figure A·1 represents a cross-section of the annulus, with $r_1$, $r_i$, $r_2$ being the radii of the inner wall, the interface, and the outer wall, respectively, Subscript A refers to the film phase, and B the bulk phase. The liquid flowrates $Q^1$ necessary to achieve the required profiles, as shown in fig. A·1, (c), (d), were calculated as follows, assuming viscous flow with no waves at the interface.

Consider a ring element of either phase
The forces acting on it are due to:

(i) Shear stress on inner surface of ring,

$$F_1 = 2\pi r.\ dz.\ \mu.\frac{\partial u}{\partial r} \qquad 2\text{-}1$$

(ii) Shear stress on outer surface of ring,

$$F_2 = 2\pi(r + dr).dz.\mu\left(\frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial r^2}\ .\ dr\right) \qquad 2\text{-}2$$

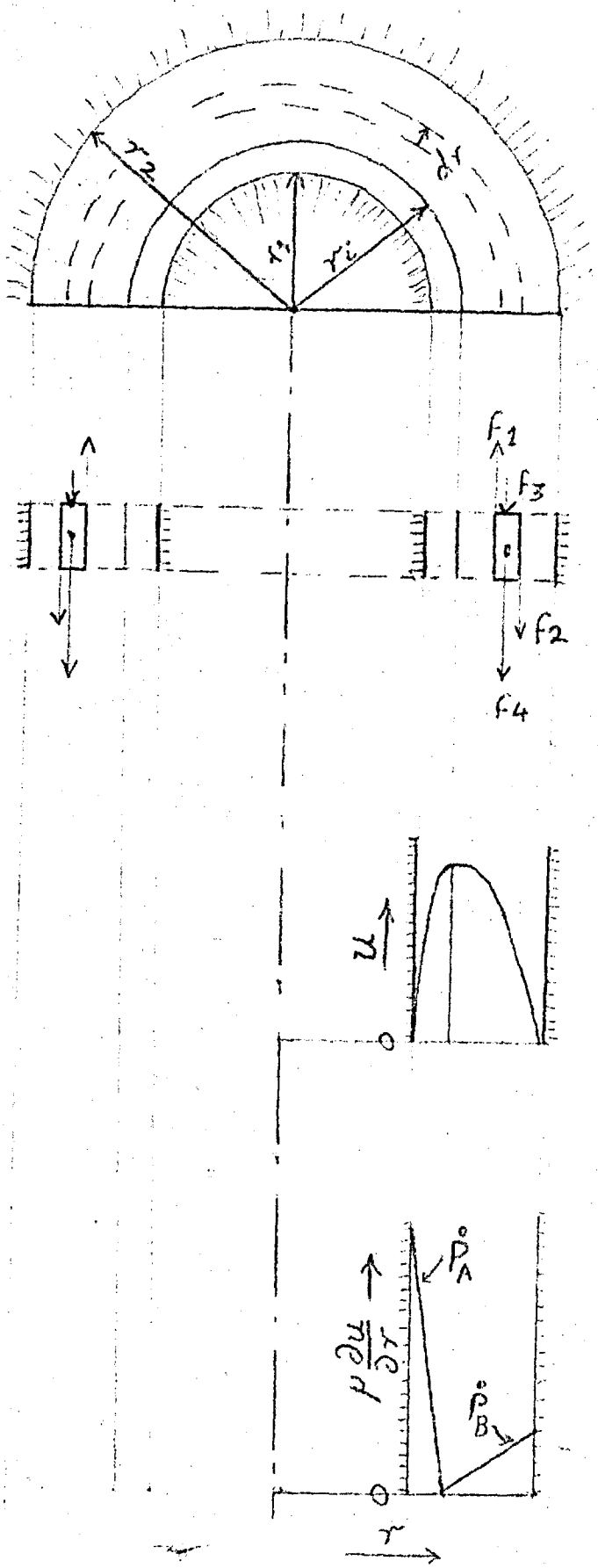
(iii) Absolute pressure gradient (apart from hydrostatic head)

$$F_3 = -\frac{dp}{dz}\ .\ dz.\ 2\pi r.\ dr \qquad 2\text{-}3$$

(iv) (Gravity) - (Hydrostatic) = (Buoyancy),

$$F_4 = (\rho - \rho_B).g.dz.\ 2\pi r.dr. \qquad 2\text{-}4$$

(Since the term $(\rho - \rho_B).g$ in $F_4$ represents a vector positive downward, dz must be measured likewise to




(a)

CROSS-SECTION OF ANNULUS

(b)

ELEMENTARY RING

(c)

VELOCITY PROFILE

(d)

VISCOUS SHEAR PROFILE

FIG. A·1

maintain consistency of sign. For cocurrent operation $F_3$ and $F_4$ always have the same sign, and may be lumped together under the "combined pressure term," $\dot{P}$, thus:

$$(F_3 + F_4) = \dot{P} = -\frac{dp}{dz} + (\rho - \rho_B).g \qquad 2\text{-}5$$

Under steady state conditions the net shear force on the ring balances the combined pressure forces:

$$F_2 - F_1 = -(F_3 + F_4) \qquad 2\text{-}6$$

Substituting from (2-1,-2,-5) in 2-6

$$\mu \frac{\partial}{\partial r}\left[r.\frac{\partial u}{\partial r}\right] = -r\dot{P} \qquad 2\text{-}7$$

Applying equation (2-7) to each of the two phases in turn:

Film Phase, A. $\dot{P}_A = -\frac{dp}{dz} + (p_A - p_B)$ 2-8

From Fig. 3(b)

$$(r_1 < r < r_i), \quad \frac{\partial u}{\partial r} > 0 \qquad 2\text{-}9$$

$$r = r_i \quad , \quad \frac{\partial u}{\partial r} = 0 \qquad 2\text{-}10$$

$$r = r_1 \quad , \quad u_A = 0 \qquad 2\text{-}11$$

The final solution of (2-7) is

$$u_A = \frac{\dot{P}_A}{2\mu_A}\left[r_i^2.\ln\frac{r}{r_1} + \frac{r_1^2 - r^2}{2}\right] \qquad 2\text{-}12$$

The total film liquid flowrate $Q_A^1$ is:

$$Q_A^1 = \int_{r_1}^{r_i} 2\pi r.u_A.dr \qquad 2\text{-}13$$

Whence, substituting for $u_A$ from 2-12 in 2-13

$$Q_A^1 = \frac{\pi\dot{P}_A}{8\mu_A}\left[4r_i^4.\ln\frac{r_i}{r_1} - (3r_i^2 - r_1^2)(r_i^2 - r_1^2)\right] \qquad 2\text{-}14$$

Mean velocity $\bar{u}_A = \dfrac{Q_A^1}{\pi(r_i^2 - r_1^2)}$ 2-15

From equation 2-12 the interfacial velocity $u_{Ai}$ is:

$$u_{Ai} = \frac{\dot{P}_A}{4\mu_A}\left( 2r_i^2 . \ln \frac{r_i}{r_1} + r_1^2 - r_i^2 \right) \quad 2\text{-}16$$

$$\frac{u_{Ai}}{\bar{u}_A} = \frac{2\left( 2\, r_i^2 . \ln \frac{r_i}{r_1} + r_1^2 - r_i^2 \right)}{\left( r_1^2 - 3r_i^2 + \frac{4r_i^4}{(r_i^2 - r_1^2)} \cdot \ln \frac{r_i}{r_1} \right)} \quad 2\text{-}17$$

By l'Hopital's rule it can be shown that equation 2-17 reduces to:

$$\frac{r_i - r_1}{r_1} \to 0 \,, \quad \frac{u_{Ai}}{u_A} \to \frac{3}{2} \quad 2\text{-}18$$

Bulk Phase, B. $\dot{P}_B = - \dfrac{\partial p}{\partial z}$ 2-19

$$r_i < r < r_2 \,, \quad \frac{\partial u}{\partial r} < 0 \quad 2\text{-}20$$

$$r = r_i \,, \quad \frac{\partial u}{\partial r} = 0 \quad 2\text{-}21$$

$$r = r_2 \,, \quad u_B = 0 \quad 2\text{-}22$$

$$u_B = \frac{\dot{P}_B}{4\mu_B}\left( 2r_i^2 . \ln \frac{r}{r_2} + \frac{r_2^2 - r^2}{2} \right) \quad 2\text{-}23$$

$$Q_B^1 = \pi \frac{\dot{P}_B}{8\mu_B}\left( (3r_i^2 - r_2^2)(r_i^2 - r_2^2) - 4\, r_i^4 . \ln \frac{r_i}{r_2} \right) \quad 2\text{-}24$$

$$\bar{u}_B = \frac{Q_B}{\pi(r_2^2 - r_i^2)} \qquad 2\text{-}25$$

$$\frac{u_{Bi}}{\bar{u}_B} = \frac{2\left(2r_i^2 . \ln\frac{r_i}{r_2} + r_2^2 - r_i^2\right)}{r_2^2 - 3r_i^2 + \frac{4r_i^4 . \ln\frac{r_i}{r_2}}{(r_i^2 - r_2^2)}}$$

Comparing the equations for the two phases, it is seen that they are identical except for differences in sign due to the inequality $r_1 < r_i < r_2$. The similarity results from the boundary condition that there should be no shear stress across the interface, so that each phase behaves as if it were an independent film moving under its own "pressure" $\dot{P}$. Thus the equations B are also similar to those derived by JACKSON [15] for a single liquid flowing down the inside of a tube. Jackson has shown that for $(r - r_i) \ll r_1$, these equations reduce to the considerably simplified case of flow down a flat wall:

$$\text{Film thickness} = \left[\frac{3\mu Q}{\dot{P}}\right]^{\frac{1}{3}} \qquad 2\text{-}27$$

Interfacial velocity

$$u_i = \frac{3}{2}\frac{Q_A}{(r_i - r_1)} = \frac{3}{2}\frac{Q_B}{(r_2 - r_i)}$$

$$= \frac{3}{2}\left(\frac{\dot{P}Q^2}{3\mu}\right)^{\frac{1}{3}} \qquad 2\text{-}28$$

2.10 Example: Film Reynolds numbers used:

$$1 < \left(Re_A = \frac{4Q_A}{\mu_A}\right) < 15$$

Above Re = 15 waves were judged to be too strong. Re = 12 corresponds to the criterion suggested by Jackson, namely that the film Froude number is 1, where

$$Fr._A = \frac{\bar{u}_A}{(gB)^{\frac{1}{2}}} = \left(\frac{R_{eA}}{12}\right)^{\frac{1}{2}}$$

at 25°C, from [27],

$\mu_{CCl_4} = 0.00888$ poise, $\rho_{CCl_4} = 1.58$ j/u

$\mu_{H_2O} = 0.00895$ poise, $\rho_{H_2O} = 0.995$ j/u

$|\rho_A - \rho_B| = 0.584 \doteq \dot{P}_A$

(since in this case $\partial p / \partial x$ is negligible)

Assuming that the apparatus is used inverted, with a water film,

$$B_{H_2O} = \frac{3 \times 0.00895}{981 \times 0.584}^{\frac{1}{3}} Q_{H_2O}^{\frac{1}{3}}$$

$$= 3.61 \times 10^{-2} \, Q_{H_2O}^{1/3}$$

$$u_i = \frac{3}{2} \frac{Q_{H_2O}}{m_{H_2O}} = 41.5 \, Q_{H_2O}^{\frac{2}{3}}$$

Hence film thickness and interfacial velocity can easily be found from log-log graphs of the above two equations.

Let $B_{H_2O} = 0.01$ cm, $u_i = 3.21$ cm,

$Q_{H_2O} = 0.021$, $Re = \frac{4Q}{\nu} = 5.5$.

In the apparatus used, $r_1 = 0.58$ cm, $r_2 = 0.70$

$$r_i = 0.58 + 0.01$$

whence, from equation 2-26,

$$\frac{u_i}{\overline{u}_B} = 1.49 \approx \frac{3}{2}$$

# - APPENDIX 2 -

## Tabulation of Results

| Runs No. | Initial Concentration | Re | t | $K_{R_R} \times 10^3$ Acid | $K_{R_R} \times 10^3$ Phenol | $\bar{F}$ Acid | $\bar{F}$ Phenol | $\bar{s}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.2,0/0,0 | 4.6 | 3.4 | 2.42 | | 2.07 | | |
| | | | 1.6 | 3.52 | | 2.61 | | |
| | | 8.0 | 5.8 | 1.85 | | 2.4 | | |
| | | | 1.3 | 3.9 | | 3.28 | | |
| | | 14.7 | 4.3 | 2.16 | | 3.1 | | |
| | | | 2.1 | 3.06 | | 3.56 | | |
| | | | 1.0 | 4.45 | | 3.77 | | |
| 2 | 0.12,0/0,0 | 4.6 | 3.4 | 2.5 | | 2.0 | | |
| | | | 1.6 | 3.65 | | 2.8 | | |
| | | 8.0 | 1.3 | 4.04 | | 3.3 | | |
| | | 14.7 | 2.1 | 3.17 | | 2.99 | | |
| | | | 1.0 | 4.6 | | 3.7 | | |
| 3 | 0.05,0/0,0 | 4.6 | 3.4 | 4.6 | | 1.75 | | |
| | | | 1.6 | 3.85 | | 2.26 | | |
| | | 8.0 | 5.8 | 2.96 | | 2.67 | | |
| | | | 1.3 | 4.25 | | 3.0 | | |
| | | 14.7 | 2.1 | 3.35 | | 3.61 | | |
| | | | 1.0 | 4.85 | | 4.13 | | |
| 4 | 0,0.05/0,0 | 4.6 | 7.1 | | 1.09 | | 1.44 | 0.26 |
| | | | 3.4 | | 1.58 | | 1.43 | 0.52 |
| | | | 1.6 | | 2.3 | | 1.88 | 2.2 |
| | | | 0.68 | | 3.51 | | 2.06 | 7.1 |
| | | 8.0 | 5.8 | | 1.21 | | 1.77 | 0.54 |
| | | | 2.7 | | 1.77 | | 1.91 | 1.4 |
| | | | 1.3 | | 2.54 | | 2.21 | 4.3 |
| | | | 0.55 | | 3.92 | | 2.46 | 12.8 |
| | | 14.7 | 4.3 | | 1.41 | | 2.19 | 1.3 |
| | | | 2.1 | | 2.00 | | 2.18 | 2.6 |
| | | | 1.0 | | 2.9 | | 3.1 | 11.0 |
| | | | 0.42 | | 4.46 | | 2.87 | 25.0 |
| 5 | 0,0.12/0,0 | 4.6 | 7.1 | | 1.06 | | 1.7 | 0.4 |
| | | | 3.4 | | 1.54 | | 1.63 | 0.75 |
| | | | 1.6 | | 2.50 | | 2.3 | 4.8 |
| | | 8.0 | 5.8 | | 1.18 | | 1.95 | 0.7 |
| | | | 2.7 | | 1.73 | | 2.0 | 1.6 |
| | | | 1.3 | | 2.5 | | 2.33 | 4.8 |
| | | 14.7 | 4.3 | | 1.38 | | 2.48 | 1.7 |
| | | | 2.1 | | 1.95 | | 2.44 | 3.4 |
| | | | 1.0 | | 2.88 | | 2.8 | 10.0 |

## Appendix 2

| Runs No. | Initial Concentration | Re | t | $K_{RR} \times 10^3$ Acid | $K_{RR} \times 10^3$ Phenol | $\bar{F}$ Acid | $\bar{F}$ Phenol | $\bar{s}$ |
|---|---|---|---|---|---|---|---|---|
| 6 | 0.0.22/0,0 | 4.6 | 7.1 | | 1.01 | | 1.85 | 0.56 |
| | | | 3.4 | | 1.47 | | 1.71 | 0.75 |
| | | | 1.6 | | 2.14 | | 2.02 | 2.9 |
| | | 8.0 | 5.8 | | 1.13 | | 2.17 | 0.82 |
| | | | 2.7 | | 1.65 | | 2.11 | 3.6 |
| | | | 1.3 | | 2.36 | | 2.43 | 5.4 |
| | | 14.7 | 4.3 | | 1.31 | | 2.62 | 1.6 |
| | | | 2.1 | | 1.87 | | 2.65 | 3.6 |
| | | | 1.0 | | 2.7 | | 3.0 | 11.0 |
| 7 | 0.2,0.05/0,0 | 4.6 | 7.1 | 1.67 | 1.1 | 1.73 | 1.57 | 0.38 |
| | | | 3.4 | 2.42 | 1.6 | 2.06 | 1.67 | 0.75 |
| | | | 1.6 | 4.45 | 2.32 | 3.7 | 2.0 | 2.7 |
| | | | 0.8 | 5.45 | 3.44 | 2.56 | 2.30 | 9.2 |
| | | 8.0 | 5.8 | 1.85 | 1.22 | 2.35 | 2.15 | 0.92 |
| | | | 2.7 | 2.72 | 1.79 | 3.10 | 1.9 | 1.34 |
| | | | 1.3 | 3.90 | 2.58 | 3.41 | 2.59 | 6.0 |
| | | | 0.55 | 6.08 | 3.84 | 2.96 | 2.73 | 16.4 |
| | | 14.7 | 4.3 | 5.0 | 1.43 | 3.2 | 2.61 | 2.0 |
| | | | 2.1 | 3.07 | 2.03 | 3.32 | 2.53 | 3.0 |
| | | | 1.0 | 4.45 | 2.9 | 3.7 | 3.32 | 14.0 |
| | | | 0.42 | 6.94 | 4.37 | 3.90 | 3.94 | 46.0 |
| 8 | 0.12,0.12/0,0 | 4.6 | 3.4 | 2.45 | 1.54 | 2.36 | 1.68 | |
| | | | 1.6 | 8.35 | 2.25 | 2.3 | 1.91 | |
| | | 8.0 | 2.7 | 2.75 | 1.73 | 2.96 | 2.0 | |
| | | | 1.3 | 3.95 | 2.50 | 2.91 | 2.42 | |
| | | 14.7 | 2.1 | 3.1 | 1.96 | 3.45 | 2.52 | |
| | | | 1.0 | 4.5 | 2.84 | 3.6 | 2.99 | |
| 9 | 0.05,0.22/0,0 | 4.6 | 3.4 | 2.5 | 1.47 | 1.99 | 1.75 | 0.52 |
| | | | 1.6 | 3.66 | 2.14 | 2.52 | 1.99 | 2.9 |
| | | 8.0 | 2.7 | 2.8 | 1.65 | 2.35 | 2.06 | 1.8 |
| | | | 1.3 | 4.04 | 2.33 | 2.8 | 2.45 | 5.4 |
| | | 14.7 | 2.1 | 3.18 | 1.85 | 3.2 | 2.61 | 3.8 |
| | | | 1.0 | 4.6 | 2.7 | 3.5 | 2.92 | 8.5 |
| 10 | 0.2,0.2/0,0 | 4.6 | 1.6 | 3.45 | 2.1 | 2.58 | 1.97 | 2.5 |
| | | 8.0 | 1.3 | 3.8 | 2.32 | 3.1 | 2.48 | 5.7 |
| | | 14.7 | 1.0 | 4.35 | 2.65 | 3.62 | 3.0 | 10.5 |

## Appendix 2

| Runs No. | Initial Concentration | t | $K_{1m} \times 10^3$ Acid | $K_{1m} \times 10^3$ Phenol | $\bar{F}$ Acid | $\bar{F}$ Phenol | $\bar{s}$ |
|---|---|---|---|---|---|---|---|
| 11 | 0.2, 0/0, 0 | 6.1 | 5.6 | 3.4 | 3.1 | 2.9 | 1.7 |
| | | 4.2 | 6.7 | 4.9 | 3.2 | 3.5 | 3.4 |
| | | 2.4 | 9.5 | 6.9 | 3.2 | 3.5 | 6.0 |
| | | 1.7 | 11.2 | 7.4 | 3.2 | 3.2 | 7.4 |
| | | 1.2 | 13.2 | 10.6 | 3.1 | 3.5 | 12.5 |
| | | 1.0 | 14.5 | 9.7 | 3.3 | 3.3 | 11.5 |
| | | 0.71 | 16.9 | 10.8 | 3.5 | 3.3 | 19.0 |
| | | 0.49 | 20.0 | 14.0 | 3.4 | 3.5 | 27.5 |
| 12 | 0, 0.05/0.5, 0 | 9.0 | 1.95 | 1.56 | | 2.0 | 0.5 |
| | | 6.3 | 3.0 | 2.2 | | 2.0 | 0.6 |
| | | 4.0 | 3.2 | 3.0 | | 1.7 | 0.7 |
| | | 5.3 | 3.2 | 2.6 | | 2.1 | 0.8 |
| | | 3.5 | 3.8 | 3.0 | | 2.0 | 1.1 |
| | | 2.4 | 4.7 | 4.4 | | 2.1 | 1.8 |
| | | 2.4 | 4.9 | 4.4 | | 2.2 | 2.0 |
| | | 1.7 | 5.7 | 4.9 | | 2.1 | 2.6 |
| | | 1.2 | 7.1 | 5.7 | | 2.1 | 3.7 |
| | | 1.0 | 6.0 | 5.3 | | 1.9 | |
| | | 0.71 | 7.9 | 7.2 | | 2.2 | 6.5 |
| | | 0.49 | 10.0 | 8.6 | | 2.3 | 7.3 |
| 13 | 0, 0/0.8, 0.2 | 8.8 | 1.5 | 1.2 | 1.1 | 1.3 | 0.2 |
| | | 2.9 | 3.2 | 2.9 | 1.5 | 1.9 | 1.3 |
| 14 | 0, 0/0.05, 0.05 | 13.8 | 0.99 | 0.86 | 0.8 | 1.1 | 0.06 |
| | | 8.8 | 1.59 | 1.53 | 1.0 | 1.6 | 0.3 |
| | | 2.9 | 2.7 | 2.7 | 1.0 | 1.5 | 0.8 |
| 15 | 0, 0/0.8, 0 | 8.8 | 1.7 | | 1.4 | | 0.8 |
| | | 2.9 | 2.9 | | 1.4 | | 0.4 |
| 16 | 0, 0/0.05, 0 | 8.8 | 1.8 | | 1.2 | | |
| | | 2.9 | 2.8 | | 1.0 | | 0 |
| 17 | 0, 0/0, 0.05 | 13.8 | | 0.8 | | 1.04 | 0 |
| | | 2.9 | | 2.7 | | 1.5 | 0.8 |
| 18 | 0, 0/0, 0.2 | 8.8 | | 1.2 | | 1.4 | 0.4 |
| | | 2.9 | | 2.3 | | 1.4 | 0.8 |

## Appendix 2

## Horizontal Extractor

| Runs No. | Initial Concentration | t | | K Acid | K Phenol | K Ratio | % Error | F | $\bar{s}$ |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 0.2,0.05/0,0 | 225 | l.m. | 1.45 | 0.93 | 1.57 | - 3 | | |
| | | | In. | 0.97 | 0.73 | 1.33 | 13 | 3.7 | 0.077 |
| | | 300 | l.m. | 1.32 | 0.75 | 1.75 | - 16 | | |
| | | | In. | 0.83 | 0.57 | 1.45 | 4 | 2.8 | 0.048 |
| | | 480 | l.m. | 1.06 | 0.52 | 2.0 | - 26 | | |
| | | | In. | 0.43 | 0.30 | 1.43 | 6 | 2.3 | 0.013 |
| | | 540 | l.m. | 1.30 | 0.55 | 2.2 | - 30 | | |
| | | | In. | 0.64 | 0.42 | 1.52 | 0 | 3.7 | 0.03 |
| | | 562 | l.m. | 0.71 | 0.35 | 2.0 | - 27 | | |
| | | | In. | 0.45 | 0.29 | 1.6 | - 5 | 2.3 | 0.01 |
| | | 780 | l.m. | 0.93 | 0.66 | 1.4 | 8 | | |
| | | | In. | 0.28 | 0.21 | 1.3 | 12 | 2.0 | 0.004 |
| 20 | 0.2,C/0,0.05 | 181 | l.m. | 1.24 | 0.96 | 1.29 | 13 | | |
| | | | In. | 0.90 | 0.70 | 1.30 | 13 | 4.5 | 0.08 |
| | | | l.m. | 0.50 | 0.33 | 1.51 | 0 | | |
| | | | In. | 0.40 | 0.28 | 1.43 | 5 | 2.8 | 0.011 |
| 21 | 0.1,0/0,0.05 | 900 | l.m. | 0.61 | 0.32 | 1.91 | - 27 | | |
| | | | In. | 0.34 | 0.22 | 1.54 | - 3 | 2.3 | 0.007 |
| | | 450 | l.m. | 0.75 | 0.36 | 2.1 | - 27 | | |
| | | | In. | 0.50 | 0.33 | 1.51 | 0 | 2.4 | 0.016 |
| | | 420 | l.m. | 0.89 | 0.43 | 2.06 | - 27 | | |
| | | | In. | 0.53 | 0.36 | 1.45 | 8 | 2.7 | 0.021 |
| | | 273 | l.m. | 0.95 | 0.39 | 2.44 | - 57 | | |
| | | | In. | 0.72 | 0.47 | 1.54 | 1 | 2.8 | 0.033 |
| 22 | 0,0/0.2,0 | 187 | l.m. | | 1.0 | | | | |
| | | | In. | | 0.81 | | | 3.8 | 0.097 |
| | | 360 | l.m. | | 0.38 | | | | |
| | | | In. | | 0.23 | | | 1.6 | 0.007 |
| | | 375 | l.m. | | 0.35 | | | | |
| | | | In. | | 0.28 | | | 1.8 | 0.008 |
| | | 473 | l.m. | | 2.5 | | | | |
| | | | In. | | 1.5 | | | 1.2 | 0.002 |
| | | 525 | l.m. | | 0.24 | | | | |
| | | | In. | | 0.14 | | | 1.1 | 0.0005 |
| 23 | 0,0.1/0,0 | 206 | In. | | 0.65 | | | 3.3 | 0.063 |
| 24 | 0,0.05/0,0 | 338 | In. | | 0.382 | | | 2.4 | 0.019 |
| | | 338 | In. | | 0.21 | | | 1.4 | 1.005 |
| 25 | 0,0.05/0.5,0 | 495 | In. | 0.22 | 0.16 | 1.41 | - 1.5 | | |

# Appendix 2

## Vertical Contactor - Surface Active Agent

| Runs No. | Concentration | t | $K_{In}$ Acid | $K_{In}$ Phenol | $K_{In}$ Ratio | % Error | $\bar{F}$ |
|---|---|---|---|---|---|---|---|
| 26 | 0.1,0.1/0,0 | 3.1 | 1.63 | 1.03 | 1.58 | - 7 | 0.69 |
| | | 3.1 | 1.31 | 0.89 | 1.47 | 0 | 0.55 |
| | | 3.1 | 1.42 | 0.93 | 1.53 | - 2 | 0.58 |
| | | 3.6 | 1.20 | 0.84 | 1.45 | 5 | 0.8 |
| | | 1.25 | 3.10 | 2.20 | 1.40 | 8 | 0.86 |
| 27 | 0.2,0/0,0.2 | 3.6 | 1.78 | 1.15 | 1.54 | 2 | 0.91 |
| | | 2.42 | 2.32 | 1.61 | 1.44 | 9 | 0.93 |
| 28 | 0,0/0.6,0.3 | 3.6 | 1.44 | 1.15 | 1.25 | 9 | 0.82 |
| | | 2.42 | 1.74 | 1.42 | 1.23 | 10 | 0.81 |
| | | 2.42 | 1.88 | 1.52 | 1.24 | 9 | 0.89 |
| 29 | 0,0.1/0.6,0 | 3.6 | 1.45 | 1.14 | 1.27 | 8 | 0.79 |
| | | 2.42 | 1.92 | 1.60 | 1.20 | 13 | 0.91 |
| 30 | 0,0.2/0.3,0 | 9.0 | 0.53 | 0.4 | 1.33 | 8 | 0.44 |

## NOTATION

(C.G.S. Units unless otherwise specified)

$a, A$ = a constant, defined in context

$B$ = film thickness

$C$ = molarity of solute, mols solute per litre of solution

$d$ = diameter

$D$ = solute diffusivity

$D_e$ = effective diffusivity, defined in equation (4-10)

$E$ = fractional extraction, Equation (4-15)

$F$ = surface renewal factor, equation (4-38)

$k$ = individual mass transfer coefficient

$K$ = overall mass transfer coefficient

$L$ = length of interface

$m$ = distribution coefficient

$N_A$ = Avogadro's number

$p$ = $Dt/B^2$, contact time criterion, equation (4-18)

$R$ = $K^{-1}$, overall resistance to mass transfer

$s$ = fractional surface renewal rate

$t$ = contact time

$x$ = axis in direction of flow

$y$ = axis perpendicular to flow

$Y(\ )$ = a function of the variables ( )

$\sigma$ = interfacial tension

Subscripts

a, A = relating to factors, a, A

C = carbon tetrachloride phase

e = see $D_e$

i = interfacial

l.m. = log. mean

0 = zero or initial value of variable

R = reference value of variable

W = water phase

Superscript

$^{x}$ = concentration driving force

$\bar{}$ = average

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